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Chapter

# Hybrid Magnetic-Semiconductor Oxides Nanomaterial: Green Synthesis and Environmental Catalytic

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## Abstract

Semiconductor oxide nanoparticles with various properties are used in applications such as photocatalysis, lithium-ion batteries, antimicrobial materials, magnetic and antibacterial materials, sensors, thermally conductive and anti-ferromagnetic films and photocatalysis. Coprecipitation, sol-gel, electrospray synthesis, laser ablation, hydrothermal and green synthesis methods have been developed for the synthesis of semiconductor oxide nanoparticles. The photocatalytic treatment method is environmentally friendly, thorough, and has high efficiency. Hybrid magnetic-Semiconductor oxide nanoparticles materials are aggregated. This results in the combination of the superparameters of the iron oxide nanosystem and the ability to rapidly adsorb pollutants and separate them from environmental water, solid. This is due to characteristic properties such as low superparameter, low toxicity, low electrical conductivity, and large specific surface area. In addition, biosynthesis has attracted attention because it takes advantage of nonhazardous, environmentally friendly biological systems like bacteria, fungi, leaves, vitamins, and yeast to synthesize metal oxide nanoparticles and combined with sonosubmersors to increase the dispersion of the system, reduce the size of the catalytic particles, and reduce the reaction time.

**Keywords:** hybrid magnetic-semiconductor nanomaterials, green synthesis, environmental catalysis

## 1. Introduction

Pollution treating technologies have been studied and applied for a long time. Up to now, they still attract a lot of attention from scientists to aim for a new material, technology with high efficiency, thorough and convenient processing. In particular, the appearance of nanomaterials has a positive impact on almost every aspect of engineering, technology and life. Environmental treatment technology is no exception to that influence. Nanotechnology involves the fabrication of nanoscale materials, along with the means and techniques to control them, in order to utilize the superior properties of this material. Nanotechnology was discovered in the late 1960s and has been

applied in many different fields from science, engineering, technology, medicine, bringing great efficiency [1]. In the field of environmental remediation, nanotechnology also promises to bring new advances. With nanomaterials having the advantage of large specific surface area, chemical activity of the surface of the material as well as the ability to transform and functionalize the surface, it opens countless research directions to bring a high performance on pollutant treatment and increase the ability to handle some stubborn pollutants. There have been many studies on this research direction, different water pollution treatment technologies have been used. In the past, the removal of pollutants often relied on adsorption technology. Accordingly, nanomaterials with adsorption affinity for pollutants are fabricated, they adsorb pollutants on the surface to help clean water flow. Of course, their limitation is that usually all materials have a certain adsorption capacity. Post-treatment material collection and an additional step of handling this material is required. A recent new direction uses materials with photocatalytic activity to combine the adsorption and treatment of organic pollutants right on the surface of the material. This type of material is usually semiconducting metal oxides, which have a wide band gap suitable for excitations by sunlight. However, nanomaterials also have disadvantages in the treatment of pollutants, especially in aqueous solution. It is because they are nano-sized that recovery will be very difficult, which easily leads to secondary contamination. To overcome this situation, scientists have thought of magnetic nanomaterials. Thanks to its magnetism, this material is easily recovered after processing.

## **2. Green synthesis of hybrid magnetic-semiconductor oxides nanomaterials**

The synthesis method plays a vital role in guiding the application of MNPs. Because this stage determines the basic properties such as particle size, size distribution, morphology, stability, and even surface properties of the MNPs. There are several different methods for synthesizing MNPs, which have been discussed in detail in many papers [2–4]. It can be observed that the common techniques used for synthesizing MNPs include coprecipitation, thermal decomposition, sonochemical, microemulsion, chemical vapor deposition, etc. In addition to these methods, a new and compatible approach to materials synthesis is using agents of natural origin such as plant extracts, bacteria, and fungi instead of chemical agents. The critical role of natural agents is as stabilizers by complexing with metal ions. Intriguingly, the natural agent-metal ion complex system reacts with the hydroxyl group in solution, forming a metal oxide instead of a metal hydroxide. This hypothesis seems plausible since metal oxides are formed at low temperatures, not by high-temperature metal hydroxide decomposition. In addition, natural agents act as capping agents, avoiding the agglomeration of nanoparticles. This approach aims to take advantage of available, renewable, natural agents and limit dependence on chemical agents to move towards a “greener” and more environmentally friendly world. Accordingly, the process of synthesizing MNPs is also done in the simplest way. It makes even more sense in environmental applications to use a “green” approach to clean the environment instead of potentially hazardous methods.

Plant extracts were the most common among the natural agents used to synthesize MNPs.

Mangosteen peel is a natural product widely used in the synthesis of nanoparticles. They are rich in phenolic compounds, flavonoids, and terpenoids. Phenolic

compounds are all potent antioxidants, while flavonoids, benzophenones, and anthocyanins are thought to be closely involved in reducing metal cations to nanoparticles [5, 6]. Yusefi et al. [7] synthesized  $\text{Fe}_3\text{O}_4$  from mangosteen peel extract, with extract concentrations varying from 0.1, 2, 5, and 10 wt.%. The results show that the obtained ferromagnetic iron oxide nanoparticles have an average size of 13.42 nm. The saturation magnetization values varied from 49.80 emu/g to 69.42 emu/g as the extract concentration increased from 0 to 10 wt.%. Nanoparticles have high stability and a long storage time. In another publication by this group of scientists, they demonstrated that the extract of *Garcinia Mangostana* fruit peel could be used as a bio-stabilizer and capping agent to enhance physicochemical properties and stability of  $\text{Fe}_3\text{O}_4$  nanofluid [8].

The peel of pomegranate (*Punica granatum L.*) is generally of no value in consumption but has been found to be highly medicinal. Several studies indicated that they contain many valuable bioactive compounds, such as polyphenols, flavonoids, proanthocyanidins, and hydrolyzable tannins [9–11]. In addition to the anti-cancer, anti-fungal, and inflammatory activities, the antioxidant activity is quite intense, which is attributed to polyphenols compounds such as punicalagin and ellagic acid. Thanks to that, it attracted many scientists' attention to synthesizing nanomaterials [12–14]. Yusefi et al. [15] synthesized magnetic iron oxide nano using Punica Granatum Fruit Peel Extract. The biologically active substances in the extract act as stabilizers, forming complexes with metal ions ( $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ). This was further confirmed when the results confirmed that a significant number of organic compounds were present in the ferromagnetic oxide mixture. The organic matter content increased gradually with the concentration of extract used. In contrast, magnetism (magnetic saturation) shows in the opposite direction. Another work has also been carried out with similar results [16].

*Lathyrus sativus* is a well-known plant that contains alkaloids, carotenoids, flavonoids, starch, carbohydrates, essential oil, leguminvicilin, legumelin, vitamin C, oleoresin, gum resin, tannins, terpenes, phenols, riboflavin, beta-carotene, proteins, and amino acids, which act as capping, reducing and stabilizing agents [17, 18]. Thanks to this unique feature, many research groups have used *L. sativus* shell extract to synthesize magnetite nanoparticles [19, 20].

Potatoes are mainly composed of carbohydrates, mostly starch. These macromolecules with hydroxyl groups are expected to facilitate metal complexation. Sharma et al. [21] used potato extract to synthesize ferromagnetic nanoparticles with the assistance of ultrasonication which facilitated quick and easy complexation.

### 3. Application of hybrid magnetic-semiconductor

#### 3.1 Removing heavy metals

Heavy metals are naturally formed in the earth's crust, they are named for their high density. Some heavy metals are common ingredients on earth such as tin, copper, gold, silver.... They are widely used in manufacturing and agriculture. Some of them are essential components of the human body, but in large doses they can be toxic, especially to children and unborn babies.

Some heavy metals are on the list of chemicals harmful to public health published by WHO including lead, cadmium, mercury, arsenic, manganese, chromium. There are different types of magnetic nanoparticles (MNPs) based on the magnetic metal



element. In heavy metal remediation field, ferromagnetic oxide attracts more attention thanks to its universality, high magnetism, low toxicity, easy synthesis, and modification.

### 3.1.1 Arsenic

Arsenic (As) is a relatively common element. They are notable for their toxicity and carcinogenic potential. Long-term use of As-contaminated drinking water will lead to cancers of the liver, lung, kidney, bladder and a number of other non-cancerous diseases related to heart, brain, diabetes [22].

In order to limit the harmful effects of As on public health, the World Health Organization (WHO) has recommended that the concentration of As in drinking water be no more than  $10 \mu\text{g L}^{-1}$ . In natural water sources, Arsenic exists in inorganic form with two main oxidation forms, arsenate  $\text{AsO}_4^{3-}$  (As(V)) and arsenite  $\text{AsO}_3^{3-}$  (As(III)). In particular, As(V) is more commonly found in surface water rich in dissolved oxygen, while As(III) is more present in groundwater. There are differences between these two existences of As. As(III) is more toxic, soluble, and mobile than As(V). However, there is a conversion process from As(III) to As(V), especially in the condition of water rich in dissolved oxygen. This process is also thermodynamically favorable, but this conversion time can also take days, weeks, or months, depending on the specific conditions [23, 24]. Various techniques can be applied to remove Arsenic such as precipitation, co-precipitation, ion exchange, adsorption, ultrafiltration, or reverse osmosis. Among these, adsorption is one of the most promising technologies because of its simple operation, low cost, and ease of research and improvement with new adsorbent materials. However, this technology is almost only effective with As(V). It is very inefficient to remove As(III), so a pretreatment process is often required to convert from As(III) to As(V) before adsorption to remove Arsenic. This process is possible using oxidizing agents or oxidizing systems. Among them, manganese dioxide emerges as a potential candidate for arsenic treatment [25, 26]. This is explained by the relatively low oxidation potential of  $\text{MnO}_2$ , which is consistent with the oxidation state of As(III) [26]. Taking advantage of this, studies on making nanomaterials from the binary metal oxide in which  $\text{MnO}_2$  and magnetic materials are combined in arsenic treatment have shown effective results. In addition to the magnetism that facilitates material recovery, iron oxides have also shown high adsorption features for As(V) [27, 28]. Zhang et al. [29] synthesized Fe-Mn binary oxide (MFM) adsorbent for arsenic treatment. The adsorbent obtained has an average particle size of  $26 \mu\text{m}$ , a specific surface area of  $265 \text{ m}^2 \text{ g}^{-1}$ , and the maximum adsorption capacity for As(V) and As(III) is  $0.93 \text{ mmol g}^{-1}$  and  $1.77 \text{ mmol g}^{-1}$ . Also, Kong et al. synthesized adsorbent materials on Fe-Mn binary oxides-loaded zeolite carriers [30]. The MFM-loaded zeolite material has good magnetism before and after arsenic adsorption. They are easily recovered by an external magnetic field. Some other characteristics such as specific surface area  $340 \text{ m}^2 \text{ g}^{-1}$ , higher than most other adsorbents used in arsenic removal, particle size distribution in the range of 20–100 nm, ratio The Mn/Fe atom is 2:9. The zeolite substrate content was varied from 10%, 20%, and 30%. The magnetic properties of the material depend on the zeolite content. Specifically, the magnetic saturation is 50.104, 31.779 and 16.165  $\text{emu g}^{-1}$ , respectively. Their coercivity forces ( $H_c$ ) are 21,307, 24,823 and 28,338 Oe, and the magnetic remanences (MR) are 2.3628, 1.8266 and 1.2903  $\text{emu g}^{-1}$ , respectively. These show that the magnetic hysteresis of the material is negligible, i.e., the magnetic field is almost zero after removing the

external magnetic field. Regarding the ability to adsorb arsenic, the test shows that almost As(III) is adsorbed on the MFM surface, gradually oxidizing to As(V). After 30 minutes of treatment, As(III) and As(V) concentrations decreased from  $2 \text{ mg L}^{-1}$  to  $3.8 \text{ } \mu\text{g L}^{-1}$  and  $6.3 \text{ } \mu\text{g L}^{-1}$ , respectively. The authors have proven that the oxidation of As (III) into As (V) is due to  $\text{MnO}_2$ , instead of Fe (II). These results show the potential application of MFM materials in arsenic treatment in water. In another work, Kumar et al. [31] synthesized magnetic nanohybrids from monolayer graphene oxide (GO) and manganese ferrite MNPs ( $\text{GO-MnFe}_2\text{O}_4$ ). The obtained adsorbent is highly magnetic, and the adsorption capacity of As(III), As(V) as well as Pb(II) are very high and significantly increased thanks to denaturation by GO.

Recently, the trend of using synthetic methods or green materials in synthesizing materials is increasingly attractive. New adsorbent materials are not out of that trend, intending to prepare inexpensive and more environmentally materials successfully. Some raw materials such as natural cellulose, biochar, and plant extracts are studied and modified with MNPs to make heavy metal adsorbents. Cellulose is a renewable biopolymer with a wide range of applications. The presence of hydroxyl groups in the main chain makes them easily modified with other materials [32]. Hokkanen et al. [33] synthesized MNPs adsorbents from modified iron oxide nanoparticles with microfibrillated cellulose. Some characteristics of synthesized adsorbent materials such as improved adsorption capacity with As(V), best adsorption conditions in a low pH environment, and experimental data show that the adsorption process follows tissue pattern. Langmuir model, the kinetics is consistent with the pseudo-quadratic model, regenerate the adsorbent with NaOH solution, after three cycles of use, the adsorption efficiency still reaches over 98%. With the same adsorbent system as cellulose iron oxide nanocomposite, Yu et al. [34] proposed a one-step synthesis method, using NaOH-thiourea-urea solution to dissolve cellulose. This method provides a “green” manufacturing process. The obtained adsorbent had good magnetic sensitivity. Its adsorption capacity for arsenite and arsenate are  $23.16$  and  $32.11 \text{ mg g}^{-1}$ , respectively. Lunge et al. [35] synthesized magnetic iron oxide nanoparticles from tea waste (MION-Tea) for arsenic removal by a straightforward method. The synthesized MNPs have a very small size, only about 5–25 nm, with a magnetization saturation value from  $6.9 \text{ emu g}^{-1}$ . The FTIR spectroscopy results indicate that traces of organic fractions of tea waste are still present on the iron oxide surface. The arsenic adsorption test gave an impressive adsorption capacity with  $188.69 \text{ mg g}^{-1}$  for As(III) and  $153.8 \text{ mg g}^{-1}$  for As(V). With a simple synthesis method, using an inexpensive tea waste agent and especially with a very high adsorption capacity of As, MION-Tea shows excellent application potential in removing As from water sources. In another interesting study by Zeng et al. [36], the iron source was obtained from iron-rich sludge water treatment. They were treated and synthesized into MNPs and re-applied to remove arsenic domestic. At pH 6.6, more than 90% of As(V) solution with a concentration of  $400 \text{ g L}^{-1}$  could be easily removed by the synthesized adsorbent ( $0.2 \text{ g L}^{-1}$ ) in 60 min. Although the maximum adsorption capacity is not ideal with about  $12\text{--}13 \text{ mg g}^{-1}$ , this is still considered a promising direction to take advantage of the wastewater filter residue to treat As in water compared to chemical agents. A similar approach is to attach ferromagnetic nanoparticles to plant-based adsorbents to add magnetism to facilitate adsorbent separation. M. Zang and his research team [37] synthesized porous biochar from woodcotton and loaded ferromagnetic nanoparticles. The material was introduced magnetic with saturation magnetization of  $69.2 \text{ emu g}^{-1}$ , which was used as an arsenic adsorbent with a reasonably good adsorption capacity, reaching  $3.147 \text{ mg kg}^{-1}$  for As(V). Similar work was done by Nham et al.

who modified biochar which was synthesized from slow pyrolysis of rice straw with  $\text{FeCl}_3$  to form a biochar material system carrying ferromagnetic nanoparticles. The results show that the magnetic addition is favorable for the separation process, and the modified biochar material also has a more significant As(V) adsorption capacity [38]. Other studies were also carried out with similar purposes but using different raw materials such as pinewood and natural hematite [39], eucalyptus extract [40], red mud [41], and agricultural biomass [42]. This result promises to provide an inexpensive, effective, and environmental solution for making arsenic adsorbents in water purification.

The arsenic adsorption mechanism on MNPs has been studied by the research group of Liu et al. [43]. They used spectroscopic techniques, including X-ray absorption near edge structure (XANES), EXAFS, and X-ray photoelectron spectroscopy (XPS), along with batch sorption experiments and thermodynamic calculations. The results show that the adsorption of As(V) and As(III) takes place very quickly at the beginning, then reaches equilibrium after about 2 hours, which is consistent with the pseudo-second-order kinetic model. The experimental data also show that As adsorption on the MNP surface is monolayer and endothermic. The results of this study are consistent with the kinetics of As adsorption on the surface of MNPs published in the above studies. The study also demonstrated that no oxidation-reduction reaction occurs on the surface of MNPs when As is adsorbed on it. Instead, oxidation-reduction reactions can slowly occur when As is exposed to the atmosphere. The size of the nanocrystalline magnetic also dramatically affects the adsorption and desorption characteristics of As(III) and As(V). Mayo et al. [44], particle size has a profound influence on the arsenic removal process. When the particle size decreased from 300 nm to 12 nm, As(III) and As(V) adsorption capacity increased nearly 200 times. It is worth mentioning that this increase is higher than the corresponding increase in specific surfaces with such a change in grain size. This result is similar to that observed in the study of Tuutijarvi et al. [45]. In their conclusion, Tuutijarvi attributed this to the fact that for particles with a size of 12 nm, their dispersion in solution is better, while with larger particles (20 nm and 300 nm, respectively) they are more easily aggregated. This explanation seems unsatisfactory. Meanwhile, J. T. Mayo's view is that the adsorption of arsenic on the surface of ferromagnetic nanoparticles is not simply adsorption on the surface of the particles but also through other means. The desorption results also support this point. Accordingly, the delay of the desorption path is more significant in the case of smaller particle sizes. The authors attributed this phenomenon to the greater affinity of arsenic for  $\text{Fe}_3\text{O}_4$  nanoparticles. This is also in agreement with previously published research results [46].

### *3.1.2 Chromium*

Chromium is a trace element that is very important for human health. However, in large doses can lead to serious health problems. Prolonged exposure to this metal can lead to higher accumulation levels in human and animal tissues, causing toxicity and impacting human metabolism, reducing crop yields [47]. Ingesting Cr-contaminated foods can lead to liver damage, lung congestion, and skin irritation. Chromium and its compounds are widely used in many industrial applications such as plating, tanning, metal finishing, photography [48]. Wastewater from these industries can contain Cr with concentrations ranging from tens to hundreds of  $\text{mg of L}^{-1}$ . Chromium exists in water mainly in two trivalent forms Cr(III) and hexavalent Cr(VI). Cr(III) is less mobile, non-toxic, and even a trace element for humans and animals to exist in this



form. In contrast, Cr(VI) is present in anionic forms as chromates ( $\text{CrO}_4^{2-}$ ), dichromates ( $\text{Cr}_2\text{O}_7^{2-}$ ), and bichromates ( $\text{HCrO}_4^-$ ). They are more mobile, highly soluble, and toxic to living organisms. In recent years, Cr pollution, especially Cr(VI) form, in both water and soil environments has increased due to human production activities. Therefore, the use of chromium in industrial production is being restricted gradually in some areas of the world. The treatment of Cr(VI) pollution in soil or water is an urgent issue, attracting much attention from scientists. Many different methods can be used to treat Cr-contaminated water. Among them, the common method is chemical redox combined with immobility. The disadvantages of this method are the prohibitive cost of the system, the consumption of chemicals, the generation of much sludge, the potential risk of re-pollution due to the leakage of sludge into the soil, and especially the recovery of metals to reuse after treatment is hardly feasible [49]. From many research results, the adsorption method has great potential for application in chromium removal, which overcomes the disadvantages of the traditional precipitation method. Shen et al. [50] synthesized  $\text{Fe}_3\text{O}_4$  of different sizes using the co-precipitation technique (8 nm) and the polgol method using propylene glycol (35 nm). The Cr(VI) adsorption efficiency was tested, and the results showed that the adsorption capacity of Cr(VI) reached 35.46 and 7.45  $\text{mg g}^{-1}$ , respectively. The effect of pH on Cr(VI) removal efficiency was investigated. As a result, a low pH value (2–3) is optimal for adsorption. This is explained by the fact that under acidic conditions,  $\text{H}^+$  ions adsorb to the adsorbent surface, making the surface positively charged, from which Cr(VI) exists in the form of oxyanions, which are readily adsorbed by interactions electrostatic action. This explanation agrees with the Cr(VI) adsorption mechanism previously proposed by Chen et al. [51]. A similar study has been done by Rajput et al. [52]. The ferromagnetic oxide nanoparticles are synthesized by the co-precipitation method. The obtained MNPs are spherical in shape, 15–30 nm in size, and the specific surface area is about 12.7  $\text{m}^2 \text{g}^{-1}$ , the point of zero charges ( $\text{pH}_{\text{PZC}}$ ) 7.4. Adsorbent materials were regenerated in an alkaline environment. Unfortunately, their adsorption capacity decreases quite quickly after each regeneration. The results of these studies show that  $\text{Fe}_3\text{O}_4$  can be used to adsorb Cr(VI), but the efficiency is not high, and the reusability is relatively poor. This can be explained because this adsorption process is physisorption, lacking the specific affinity of Cr(VI) for  $\text{Fe}_3\text{O}_4$ . In addition, the medium favors the adsorption of Cr(VI) under low pH, which easily leads to the dissolution of  $\text{Fe}_3\text{O}_4$ . Therefore, the study and enhancement of the adsorption capacity of  $\text{Fe}_3\text{O}_4$  for Cr(VI) by denaturing, increasing the specific surface area, or introducing organic species with a particular affinity for this metal are being studied.

The research group of Shi et al. [53] attached  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  to carboxylated biochar to form magnetic biochar to remove Cr(VI) and Cr(III) metals in the solution acid. The results show that  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  not only enhances the adsorption capacity of Cr(VI) anions but also immobilizes Cr(III) cations. The proposed process mechanism consists of 3 steps: (1) adsorption of Cr(VI) anions on the surface by protonated functional groups; (2) reduction of the Cr(VI) anion to the Cr(III) cation by electron donor groups; (3) complexation and immobilization of Cr(III) by amine and carboxyl groups on magnetic biochar.

Polypyrrole (PPy) is an organic polymer synthesized by oxidative polymerization of pyrrole. PPy possesses many interesting properties such as high electrical conductivity, environmental stability, non-toxicity, and ease of preparation. These advantages make PPy very popular in many different applications [54, 55]. PPy is noted to be positively charged at the N atoms on the main chain, which is highly preferred in synthesizing adsorbents [56]. The PPy/ $\text{Fe}_3\text{O}_4$  nanocomposite adsorbent



was first synthesized by Bhaumik et al. to remove Cr(VI) [57]. The ferromagnetic nanoparticles were encapsulated by PPy through the in-situ polymerization of the pyrrole monomer. The removal efficiency of Cr(VI) was very high, reaching 100% with a 200 mg/L Cr(VI) solution at pH 2. The team also proposed that the main mechanism in Cr(VI) adsorption is the reduction and ion exchange on the PPy/Fe<sub>3</sub>O<sub>4</sub> nanocomposite surface. The adsorbent also showed the ability to reuse after two cycles of adsorption-desorption with almost no reduction in the adsorption capacity. The research group of Wang et al. [58] have synthesized a tertiary magnetic nanocomposite consisting of reduced graphene oxide (rGO), polypyrrole (PPy), and Fe<sub>3</sub>O<sub>4</sub> nanoparticles (PPy-Fe<sub>3</sub>O<sub>4</sub>/rGO) for Cr(VI) removal application. The material's magnetism has been evaluated, showing a significant reduction in saturation magnetization value compared with Fe<sub>3</sub>O<sub>4</sub>/rGO. The Cr(VI) removal efficiency increased significantly after the Fe<sub>3</sub>O<sub>4</sub>/rGO nanocomposite was modified with PPy by an in situ polymerization. The results of surveying the influence of foreign ions showed that cations such as Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and anions such as Cl<sup>-</sup>, and NO<sub>3</sub><sup>3-</sup> hardly affect the removal efficiency of Cr(VI). However, the presence of SO<sub>4</sub><sup>2-</sup> anion inhibited Cr(VI) adsorption.

### *3.1.3 Simultaneous removal of multiple other heavy metals*

In addition to chromium and arsenic, magnetic nanomaterials have been studied for the simultaneous removal of many other heavy metals. This aspect of research is interesting and has significant practical implications. Because, in practice, wastewater cannot exist as a single metal cation, they are always a complex mixture. The studies also tested the effects of impurities, including other metal ions commonly found in water sources such as Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> cations, or anions such as Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>. Several studies have also conducted surveys to evaluate the effect of organic species on the removal efficiency of heavy metals.

Liu et al. [59] synthesized humic acid (HA) coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles by co-precipitation method to remove some heavy metal ions such as Hg(II), Cd(II), Cu (II). The results show that the Fe<sub>3</sub>O<sub>4</sub>/HA material system is nano-sized with a Fe<sub>3</sub>O<sub>4</sub> core of approximately 10 nm. In solution, they form particles with hydrodynamic sizes up to 140 nm. Their magnetic saturation is relatively high with 79.6 emu g<sup>-1</sup>, which makes them easily recovered by an external magnetic field in a short time. The tests also show that Fe<sub>3</sub>O<sub>4</sub>/HA has high stability in tap water, natural water, and acidic environments from 0.1 M HCl to alkaline 2 M NaOH with low leaching (Fe ≤ 3.7%; HA ≤ 5.3%). The removal efficiency of heavy metals of Fe<sub>3</sub>O<sub>4</sub>/HA material system compared to Fe<sub>3</sub>O<sub>4</sub> in other publications has been significantly enhanced. Specifically, the removal efficiency is up to over 99% for Hg(II) and Pb(II) and over 95% for Cu(II) and Cd(II) in tap water at optimum pH. The desorption of these metals to an aqueous medium is not significant. This shows the ideal potential of the Fe<sub>3</sub>O<sub>4</sub>/HA material system in treating polluted heavy metals in water sources. In another study, Ge et al. [60] synthesized Fe<sub>3</sub>O<sub>4</sub> nanoparticles by co-precipitation method that followed functionalizing surface with a 3-aminopropyltriethoxysilane (APS) agent and then attaching a copolymer of acrylic acid and crotonic acid (AA-co-CA) tail. The material has a uniform size of 15–20 nm, saturation from 52 emu g<sup>-1</sup>, and slightly lower with Fe<sub>3</sub>O<sub>4</sub> of 79.67 emu g<sup>-1</sup>. Fe<sub>3</sub>O<sub>4</sub>@APS@AA-co-CA is used to remove heavy metal ions (Cd<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup>, and Cu<sup>2+</sup>) from an aqueous solution. Experimental results show that the synthesized adsorbent is highly effective with Pb<sup>2+</sup> and Cu<sup>2+</sup> ions. Their adsorption capacity reaches 166.1 mg g<sup>-1</sup> and 126.9 mg g<sup>-1</sup>, respectively. For Cd<sup>2+</sup> and

$\text{Zn}^{2+}$ , the adsorption capacity was lower,  $29.6 \text{ mg g}^{-1}$  and  $43.4 \text{ mg g}^{-1}$ , respectively. The limitation of this study is that the method and conditions for the adsorbent regeneration have not been specified. However, the authors have stated that a pH lower than two causes this material to be inactive.

The iron oxide nanomaterial facilitates quick and easy recovery of the adsorbent. However, they have the disadvantage that the chemical activity is quite sensitive. Iron oxides are easily dissolved in an acidic environment, leading to ineffective pollutant removal. Therefore, when using ferromagnetic as a pollutant treatment agent, it is necessary to take accompanying measures to enhance the durability and stability of this material. Especially in the heavy metal elution situation, regeneration of the adsorbent is usually carried out in an acidic medium. A core-shell structure magnetic nanomaterial  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  was synthesized by Wang et al. [61]. The layer of  $\text{SiO}_2$  with acid resistance is used as a protective shell for  $\text{Fe}_3\text{O}_4$  ferromagnetic cores. In addition,  $\text{SiO}_2$  rich in hydroxyl groups on the surface also helps to facilitate the functionalization of organic agents. The obtained  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  had a specific surface area  $216.2 \text{ m}^2 \text{ g}^{-1}$ , average size 18.4 nm. This material has high stability in an acidic environment. The solubility of Fe in 1 M HCl solution after 24 h is only 1.57%, much lower than 90.7% of bare  $\text{Fe}_3\text{O}_4$ . The adsorption capacity, affinity for heavy metal cations including Cu(II), Pb(II), and Cd(II), as well as the influence of pH, and foreign electrolytes, were evaluated. The results show that this material has good strength, high selectivity, and the ability to regenerate by acid agent (1 mol/L HCl acid solution) are all very effective. In particular, experiments show that after adsorption of energetic metals,  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  is easily recovered quickly by an external magnetic field.

Some organic species that have the advantage of complexing with heavy metal ions are also used to modify the surface of nanoparticles with the expectation of high efficiency in heavy metal removal. Among them attracting much attention from researchers is ethylene diamine tetraacetic acid (EDTA). Liu et al. [62] synthesized core-shell magnetic nanomaterials based on  $\text{Fe}_3\text{O}_4$ , and the surface of the  $\text{SiO}_2$  shell was directly modified with EDTA with the ratio of  $\text{Fe}_3\text{O}_4:\text{SiO}_2:\text{EDTA}$  components instead. In which the ratio of these components 2:5:1 gives the best adsorption capacity. Some characteristics of this material include a specific surface area of  $24.07 \text{ m}^2 \text{ g}^{-1}$ , an average pore size of 15.40 nm, a total pore volume of  $0.09 \text{ cm}^3 \text{ g}^{-1}$ , and saturation magnetization from  $34.49 \text{ emu g}^{-1}$ . Evaluating the effects of other metal cations such as  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and natural organic matter (NOM) such as humic acid and sodium alginate had proved that the  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-EDTA}$  material had high selectivity for heavy metals such as Pb(II) and Cu(II). In another study, Ren et al. used EDTA as an affinity enhancer for heavy metal ions [63]. Accordingly, the magnetic nanostructure with core-shell structure  $\text{Fe}_3\text{O}_4\text{-SiO}_2$  was surface modified with chitosan before being added with EDTA tail. The descriptive results show that the magnetic adsorbent has a size from 200 to 400 nm, and specific surface area, pore diameter, and pore volume are  $1.04 \text{ m}^2 \text{ g}^{-1}$ , 8.28 nm, and  $2.2 \times 10^{-3} \text{ cm}^3 \text{ g}^{-1}$ , respectively. The acid stability of the synthesized adsorbent was significantly enhanced after surface modification with chitosan and EDTA. Specifically, after soaking for 12 hours in 1 M HCl solution, the solubility of  $\text{Fe}_3\text{O}_4$  of  $\text{SiO}_2/\text{Fe}_3\text{O}_4$ , functionalized chitosan  $\text{SiO}_2/\text{Fe}_3\text{O}_4$  (CMS), and EDTA-modified CMS (EDCMS) were 1.28%, 1.02%, and 0.77%, respectively. The saturation magnetization of the materials after the modification steps of  $\text{Fe}_3\text{O}_4$  microspheres,  $\text{SiO}_2/\text{Fe}_3\text{O}_4$  microspheres, CMS and EDCMS are 69.0, 56.3, 20.7, and  $18.2 \text{ emu g}^{-1}$ , respectively. There is a decrease in magnetic saturation after each step of material modification. This phenomenon is also explained similarly to the previous

studies, as the mass content of magnetic  $\text{Fe}_3\text{O}_4$  decreases with each addition of other agents. Although the magnetic saturation is reduced, they are still large enough to facilitate the separation of the nano adsorbents from the aqueous medium quickly and easily by the external magnetic field. The results of the heavy metal adsorption test showed that the nano adsorbents particles whose surfaces were modified by EDTA gave the adsorption capacity for  $\text{Cu(II)}$ ,  $\text{Pb(II)}$ , and  $\text{Cd(II)}$  0.699, 0.596, 0.563  $\text{mmol g}^{-1}$ , respectively. While for undenatured chitosan  $\text{SiO}_2\text{-Fe}_3\text{O}_4$  (CMS) nanoparticles, these values are only 0.495, 0.045, 0.040  $\text{mmol g}^{-1}$ . This enhancement is attributed to the presence of EDTA, which provides ease of complexation of metal ions. Zhang et al. [64] synthesized magnetic nanomaterials for mercury adsorption in the aqueous medium. Accordingly, the  $\text{Fe}_3\text{O}_4$  magnetic cores are surrounded by  $\text{SiO}_2$  shells and attached to thiol ( $-\text{SH}$ ) bridges on their surface. This design is built based on Pearson's acid-base theory [65], in which mercury belongs to the group of soft acids, meaning that they quickly form strong bonds with soft Lewis base groups such as  $-\text{CN}$ ,  $-\text{RS}$ ,  $-\text{SH}$ . The results show that the  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SH}$  material is nanoscale, with an average diameter of about 10 nm despite having a large size dispersion. Magnetic redundancy and reluctance are almost zero. Magnetic saturation is relatively high, 55.05, 25.45, and 20.47  $\text{emu g}^{-1}$  correspond to  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ , and  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SH}$ . The study on mercury adsorption capacity showed that this material has a large adsorption capacity with mercury, even under changing pH of the solution. Especially under low pH conditions, with competitive adsorption of  $\text{H}^+$  and other cations such as  $\text{K}^+$ ,  $\text{Na}^+$ , and  $\text{Ca}^{2+}$ , the mercury adsorption capacity remained at a high level, 110  $\text{mg g}^{-1}$ .

### 3.2 Degradation of organic pollutants

Organic pollutants are toxic organic compounds that cause human health problems and diseases when residues exceed permissible limits. Industrial products such as detergents, organic solvents, dyes, pesticides, or some organic pollutants, which are biochemical products of bacteria, fungi, and mainly algae secreted, etc., are toxic and carcinogenic. They can exist in different forms in environments where typical physicochemical or biological techniques have become ineffective in removing them [66, 67].

Magnetic adsorbents are usually designed in a core-shell structure. Magnetite nanoparticles will have a core of magnetic material and a shell that adsorbs and treats pollutants outside. Zhang and Kong [68] have synthesized  $\text{Fe}_3\text{O}_4/\text{C}$  magnetic adsorbent in which the carbon (C) adsorbent layer is covered on the surface of the magnetic nanoparticle. The synthesized nanoparticles, which have an average diameter of about 250 nm, are good dispersion in aqueous media and are quickly and easily separated by external magnetic fields. The adsorption efficiency was tested with MB and CR pollutants. The adsorption capacity of  $\text{Fe}_3\text{O}_4/\text{C}$  for these pollutants was 44.38  $\text{mg g}^{-1}$  and 11.22  $\text{mg g}^{-1}$ , respectively.

Microcystins (MCs) are a class of toxins produced by certain species of freshwater cyanobacteria, commonly known as blue-green algae. There are more than 50 different compounds belonging to this group. They are disocyclic heptapeptides with a molecular weight of about 1000 Da, such as MC-RR, MC-YR, and MC-LR. Among them, MC-LR is the most popular. Microcystin belongs to a group of toxins that are very dangerous to humans, livestock, and pets if ingested [69]. In order to remove them from water, methods such as coagulation and mechanical filtration can be used, but only the insoluble particles are removed. For dissolved poisons, activated carbon



can be used, but effective removal of MC requires a large amount of activated carbon adsorbent. With chemicals for chlorination or ozonation, there are similar limitations. In addition, using these methods carries the risk of creating secondary toxic products [70]. Deng et al. [71] synthesized mesoporous microspheres, sandwich structures of approximately 500 nm in size, to treat this type of organic poison. In this study, the core-shell structure  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  was fabricated by the sol-gel method. The porous structure of the shell is formed by a composite layer of cetyltrimethylammonium bromide (CTAB) and silica after the removal of CTAB by acetone extraction. As a result, this porous shell has a uniform diameter, about 70 nm thick. The authors also proved that these porous capillaries have a direction perpendicular to the material's surface. The pore size is about 2.3 nm, the specific surface area is  $365 \text{ m}^2 \text{ g}^{-1}$ , and the total pore volume is  $0.29 \text{ cm}^3 \cdot \text{g}^{-1}$ , magnetic saturation is  $53.3 \text{ emu g}^{-1}$ . MC treatment results show that with a relatively low dose, about  $0.05 \text{ mg } \mu\text{g}^{-1}$ , the adsorbent can remove MCs in solution, and the removal efficiency is more than 95%. After extraction with acetonitrile/water mixture regenerates, the adsorbent can be reused with MC removal efficiency above 90% after eight cycles of use. This result shows that the magnetic material synthesized by the research team has very high efficiency in removing toxic MCs, convenient recovery and regeneration, can be reused many times, and is effective in economic and technical aspects.

Recently, photocatalysis technology has received significant attention for treating polluted organic compounds. Photocatalysis uses the excitation energy from sunlight to decomposing organic compounds into harmless products of  $\text{CO}_2$  and water or other particles along the water flow. Their advantages are that they do not use additional treatment chemicals, do not generate secondary pollution products, and the toxic organic compounds are always decomposed on the catalyst surface without having to be recovered for treatment at another step [72, 73]. However, like in heavy metal treatment, the catalyst material must also be recovered to avoid environmental emissions. Therefore, synthesizing materials with both photocatalytic activity and magnetism to facilitate recovery and treatment has attracted significant attention from researchers.

In a publication by Chi et al. [74], the research team synthesized magnetic nanomaterials doped by active silver metal centers, which are catalysts for 4-nitrophenol (4-AP) treatment. With the help of polyvinylpyrrolidone (PVP) as a reducing agent and stabilizing agent, the synthesized  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$  composite material has a spherical shape, a core size of about 200 nm, and a  $\text{SiO}_2$  shell. The average thickness is about 35 nm, and the size of Ag NPs is controlled at about 3.65 nm and is evenly distributed on the  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  background. The magnetism of the materials is not significantly reduced compared to the magnetic core, whereby the magnetic saturation of  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ , and  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$  is 78.5, 66.4, and  $63.8 \text{ emu g}^{-1}$ , respectively. The treatment efficiency of 4-AP is excellent. The rate constant of this compound degradation is higher than that of some Ag catalysts carried on other substrates published previously. The catalytic activity of the material was also maintained stably after eight treatment cycles. The 4-AP conversion still reached over 99%. After that, a decrease in activity was initiated, but this was negligible.

Titanium oxide is considered one of the materials that was attracting much attention in its use as photocatalysts in treating organic pollutants. It has high chemical and biological inertness and solid oxidizing force. The main disadvantage of these metal oxides is that they have a reasonably wide band gap, about 3.2 eV, which means that their excitation energy must be ultraviolet radiation, not radiation in the visible region. In addition, poor recovery efficiency is also one of the limitations of this



material. Many studies used magnetic metals/metal oxides integrated with  $\text{TiO}_2$  to facilitate the recovery of this material after treatment. Mortazavi-Derazkola et al. [75] synthesized a core-shell magnetic photocatalyst  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TiO}_2@\text{Ho}$  to treat rhodamine B and methyl orange dyes under UV radiation conditions. This catalyst material is synthesized from the magnetic core  $\text{Fe}_3\text{O}_4$  covered by the  $\text{SiO}_2$  shell. This  $\text{SiO}_2$  shell, which protects the  $\text{Fe}_3\text{O}_4$  core from acid attacks, is also used to add silane coupling agents to facilitate the deposition of  $\text{TiO}_2$  on the surface. Holmium (Ho) is doped onto the surface of the adsorbent, which acts as electron traps to separate the electron-hole by creating local electric fields. The descriptive results show that the particle size of  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TiO}_2@\text{Ho}$  is about 52 nm, the outermost Ho shell is about 3 nm thick, and the  $\text{TiO}_2$  NPs layer is 3.5 nm thick. Their saturation magnetism decreased quite deeply after coating many outer shells of the  $\text{Fe}_3\text{O}_4$  magnetic core. Specifically, the saturation magnetization decreased from 57.42 to 24.5  $\text{emu g}^{-1}$  when coated with  $\text{SiO}_2$ . This value decreased to 15.9 and 6.2  $\text{emu g}^{-1}$  when  $\text{TiO}_2$  and Ho were coated, respectively. Although the saturation magnetization is relatively low, they are still sufficient to separate the adsorbent from the aqueous solution by an external magnetic field. Testing the ability to handle pollutant compounds rhodamine B and methyl orange showed that under dark conditions, without UV irradiation, this material only adsorbs up to 4% of organic pollutants in the water solution. Meanwhile, with an irradiation time of more than 2 h, the decomposition efficiency of Rhodamine B and Methyl Orange was 92.1% and 78.4%. In particular, this type of catalyst is readily regenerated by washing with clean water and ethanol and used again after being recovered by an external magnetic field. After each cycle of use, the catalytic activity and the degree of conversion decreased very little. This stable shows a great potential application of this material in treating organic dyes that pollute water sources. Zinc oxide (ZnO) is a semiconductor with unique properties such as a stable hexagonal wurtzite structure and a wide band gap of 3.37 eV, which is the large binding energy of 60 meV at room temperature. Hence, ZnO possesses some unique abilities, such as bactericidal properties and photocatalytic activity [76, 77]. Studies on the ability in water treatment, photocatalytic activity, the influence of factors such as doped element, synthesis method, particle size, etc. were published [78–81]. However, in order to lead to a possible practical application, magnetic nanomaterials based on ZnO have been thought of as a means of increasing the ability to recover and reuse this potential material. The Fe-Zn binary oxide material was synthesized by Kumar et al. [82]. The optical, magnetic, and photocatalytic properties and the influence of Fe-doped content in methylene blue (MB) dye treatment were evaluated. The survey results show that Fe-Zn binary oxide has enhanced photocatalytic performance compared to simple ZnO under UV radiation and sunlight. The magnetism of this material was found to be dependent on the Fe dose. Similar material was studied by Falak et al. but with a specific and more Fe content [83]. A magnetic ZnO-ZnFe<sub>2</sub>O<sub>4</sub> binary composite was created by the research team. The catalytic activity of this composite was also studied on MB. The results show more than 40% of their catalytic activity compared to ZnO nanoparticles. In addition, the magnetization saturation value of ZnO-ZnF<sub>2</sub>O<sub>4</sub> was about 5.8  $\text{emu/g}$ , which is high enough that they can be collected by applying an external magnetic field. In another study, Boutra et al. [84] synthesized a nanocomposite photocatalyst from ZnO, manganese ferrite ( $\text{MnFe}_2\text{O}_4$ ), and tannic acid (TA) by hydrothermal method. The photocatalytic activity was evaluated through its ability to decompose Cong Red (CR) under visible light irradiation. The results showed that CR decomposition efficiency reached 84.2%, higher than simple ZnO. The catalyst is easily separated and reused without even washing, drying,

or any other technique to remove CR. The performance after the fifth reuse remains high, up to 77.5%. Dlugosz et al. [85] synthesized Fe<sub>3</sub>O<sub>4</sub>/ZnO magnetite nanoparticles and tested their photocatalytic activity on series of organic dyes, including MB, MO, Quinoline Yellow, Eriochromic Black T (EBT), and Trypan Blue (TB). The synthetic magnetic nanomaterial is 30% Fe<sub>3</sub>O<sub>4</sub> by mass, with saturation magnetization of about 9.5 emu/g. The recovery of Fe<sub>3</sub>O<sub>4</sub>/ZnO reached 83.91%, slightly lower than Fe<sub>3</sub>O<sub>4</sub> (94.80%). Notably, the catalytic activity of this material was found to increase with the molecular weight of the dye. Specifically, the photodegradation efficiency of Fe<sub>3</sub>O<sub>4</sub>/ZnO reached 76.90% for TB (872.9 g/mol), 63.02% for EBT (461.4 g/mol) and 13.23% for MB (319.9 g/mol). We have studied the synthesis of (polyethylene glycol)–Fe<sub>3</sub>O<sub>4</sub>/ZnO material [86]. The main objective of this study is the preparation of a PEG (polyethylene glycol)–Fe<sub>3</sub>O<sub>4</sub>/ZnO magnetic nanocomposite using a green sonochemical synthesis method with rambutan peel extract as a stabilizing agent for photocatalytic methylene blue degradation. The result showed the size of nanocomposite was 20–30 nm and had the band gap energy of 2.58 eV. Measurements of the degradation efficiency of the photocatalyst showed that the photocatalytic degradation of methylene blue follows pseudo-first order kinetics with good correlation and linear regression coefficient. This study found that the maximum degradation of the methylene blue dye was approximately 96%, with pH = 4.0, a PEG–Fe<sub>3</sub>O<sub>4</sub>/ZnO concentration of 1.0 g L<sup>-1</sup>, a methylene blue concentration of 200 mg L<sup>-1</sup>, and a time of 90 min. In the dark, the Langmuir adsorption constant and the maximum adsorbable methylene blue quantity were calculated as  $K_L = 0.0451 \text{ L mg}^{-1}$  (and  $K_L = 11.275K_{LH}$ ) and  $Q_{max} = 21.05 \text{ mg g}^{-1}$ . This study concludes that for the Fe<sub>3</sub>O<sub>4</sub>/ZnO magnetic nanocomposite, the adsorption process supports catalytic methylene blue degradation, reducing the decomposition time, increasing the efficiency of the catalytic process, and increasing the sample recovery due to the magnetic properties of the material.

From these research results, integrating ferromagnetic oxide nanoparticles into ZnO will yield a new magnetic material. The degree of magnetism will usually depend on the Fe<sub>3</sub>O<sub>4</sub> content in the material. Therefore, in practice, if the material must achieve certain levels of magnetism in order to facilitate a particular separation requirement, consideration should be given to adjusting the mass ratio of this component in the material. In addition, in the presence of Fe<sub>3</sub>O<sub>4</sub>, the photocatalytic activity of the material increases quite significantly.

#### 4. Conclusion and outlook

It can be seen from the summarized statements that using “green” agents to fabricate materials is a possible route. However, many studies have shown that the efficiency in both the reaction yield and the properties of the obtained MNPs is very impressive, the plant source is immense, and scientists still need to do more research to improve the effectiveness and activity of MNPs products.

The results show that integrating a sufficiently large amount of Fe<sub>3</sub>O<sub>4</sub> will make the composites magnetic enough to separate them from the aqueous solution by an external magnetic field. This characteristic is significant, overcoming the inherent disadvantage of nanomaterials which disperse too well to be challenging to recover. Since then, this defect has been resolved smoothly. Recent studies have also considered the applicable conditions closer to reality when the effects of cations, anions, and natural organic matter (NOM) are thoroughly investigated and evaluated. In addition, with many contaminants such as arsenic, and several organic pollutants,

ferromagnetic oxide not only acts as a recovery aid but also enhances the treatment efficiency thanks to its unique properties. The summarized research results also show an excellent combination between a magnetic metal oxide and a semiconductor metal oxide, which plays a crucial catalytic role in the photodegradation of pollutant compounds, especially organic pollutants. Some studies have shown the mechanism of the entire treatment process, including the adsorption of pollutants on the material's surface and the photodegradation reaction taking place at the catalytic sites under the catalysis activation of UV radiation or visible light.

## **5. Conclusion**

In this chapter, a small portion of the space is devoted to reviewing green methods using plant-based agents to prepare MNPs.

The rest of the chapter is devoted to generalizing the results of research on synthesizing magnetic nanomaterials, mainly ferromagnetic oxides, to remove pollutants such as heavy metals, toxic substances, etc. organic pollution.


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