

APPROACH OF TRANSITION METAL CATALYSTS IN PURIFICATION OF WASTE WATER

Abstract

In today's era, water scarcity is one of the major issues to be dealt with. Among various methods developed for wastewater treatment adsorption technique has proved to be a very effective and sustainable tool. The present chapter deals with the use of transition metals as catalysts for a total solution to the complex problem of wastewater treatment. Various transition metals such as iron, copper, nickel, manganese, Palladium, Titanium, and cobalt due to their distinctive electronic properties which are because of the presence of d-orbital have been utilized for wastewater treatment by oxidative and reductive mechanisms. A detailed elaboration of different processes used and metal catalysts like a platinum catalyst, copper oxide zinc oxide, iron oxide, tungsten trioxide, etc has been discussed. Additionally, various recovery and regeneration techniques of spent adsorbents including filtration, centrifugation, and magnetic separations are discussed in detail. Therefore, the unique properties and versatility of transition metals in catalyzing pollutant degradation processes position them as powerful tools for improving waste water management strategies.

Keywords: Wastewater, Metal catalysts, Pollutant degradation

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I. INTRODUCTION

Environmental degradation and shortage of water have been one of the most sensitive issues today, due to our rapidly expanding global population and economic development. India and many other countries, is experiencing worst droughts in its history which is an alarming situation. Water scarcity is increasing day by day, creating the situation that the country is almost on the verge of losing all its fresh water. Demand for freshwater is rising to a peak with industrial activities, agricultural development, and domestic uses. [1] Effective treatment and reuse of wastewater is indeed a crucial aspect of sustainable water management.

Wastewater is any water that has been adversely affected in quality by anthropogenic influence which includes water from domestic, industrial, commercial, or agricultural activities. Wastewater encompasses a broad range of potential contaminants and concentrations, depending on its source. It can include water from sources such as sinks, showers, toilets, washing machines, and dishwashers. Sewage typically contains a mix of physical, chemical, and biological contaminants including human waste, soaps, detergents, food scraps, oils, and other organic materials. Wastewater treatment process manages to remove contaminants from used water. [2-3] as it is very essential for environmental protection and maintaining public health. Wastewater if untreated, contains various types of pathogens, organic pollutants, industrial wastes and heavy metals that are major source of adulteration of drinking water sources which are responsible for causing many non-curable diseases.

Wastewater can also come from livestock operations, in the form of animal waste or the excessive use of antibiotics. In aquaculture, wastewater may contain excess feed, waste products, and chemicals used to treat diseases. Discharging untreated wastewater directly into the environment leads to the degradation of aquatic ecosystems, the depletion of water bodies, and the accumulation of harmful pollutants in the environment. Therefore, treatment of wastewater is a topic of interest in order to reduce the risk of waterborne diseases and in favour of public health protection and to balance the ecosystems. [4-5] Reusing the treated wastewater provides an alternative, reliable source of water, which also known as water recycling.

This includes irrigation, industrial processes, groundwater recharge, and even direct potable reuse after appropriate treatment levels. Water reuse reduces the demand for freshwater, thereby conserving limited freshwater resources. It provides a reliable water supply, especially in dry regions or during periods of drought. It can also reduce the energy usage and environmental pollution associated with extracting and transporting freshwater. The reuse of wastewater also present technical challenges related to ensuring the treated wastewater meets the quality standards for its intended use, economic challenges related to the cost of advanced treatment processes, and social challenges related to public acceptance. [6] Sewage can also contain pathogens, including bacteria, viruses, and parasites that can cause diseases. [7-8] Runoff from roads is also known as storm water runoff, this is water from rain or melting snow that flows over the ground surface and pick up pollutants such as oils, heavy metals, pesticides, fertilizers, and litter from roads and other paved surfaces that can lead to water pollution if it is not effectively managed and treated [9].

Agricultural waste includes runoff from fields, which can carry soil, organic matter, and agrochemicals such as fertilizers and pesticides. Agricultural wastewater can cause eutrophication, destroy aquatic life, and contaminate drinking water sources if it is not adequately handled. [10] Industrial wastewater refers to wastewater produced from industrial activities. The nature of these wastes can vary widely depending on the industry. For example, the textile industry may produce wastewater containing dyes and solvents, the metal industry may produce wastewater containing heavy metals, and the food and beverage industry may produce wastewater high in organic matter. Untreated or improperly treated industrial wastewater can have severe impacts on both human health and the environment. [11] Properly treating and managing wastewater is crucial for protecting human health, preserving the environment, and ensuring the sustainability of our water resources. Which can prevent pollution, disease transmission, and the degradation of ecosystems, while also reclaiming valuable resources and contributing to water security.

The effective treatment of wastewater can transform it from a potential hazard into a valuable resource. It is typically characterized by various contaminants, each posing distinct threats to both the environment and public health. Heavy metals such as lead, mercury, arsenic, and cadmium are common contaminants often found in wastewater. They originate from various industrial processes and improper disposal of consumer products. These metals are not biodegradable and tend to accumulate in the environment and living organisms, leading to severe health problems such as neurological disorders and cancer. [12] Organic pollutants include various compounds such as pesticides, pharmaceuticals and dyes. These compounds can be resistant to conventional treatment methods, leading to their accumulation in water bodies.

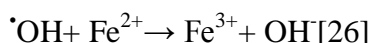
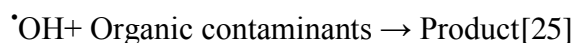
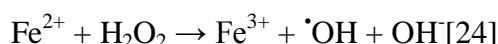
They can have harmful effects on aquatic life and can also pose risks to human health if they contaminate drinking water sources. [13] Pathogens, including bacteria, viruses, and parasites, are biological agents that can cause diseases. They commonly enter wastewater through sewage and untreated human waste. These pathogens can cause a range of diseases, such as cholera, dysentery, and typhoid, posing a significant public health risk. [14] The development and implementation of innovative and sustainable wastewater treatment technologies are of paramount importance. Among the various techniques being explored, the utilization of transition metals as catalysts in wastewater treatment processes offers considerable promise. In recent years, the use of transition metals as catalysts has emerged as a promising solution to the complex problem of wastewater treatment. Transition metals, including elements such as iron, [15] copper, [16] nickel, [17] manganese, [18] Palladium, [19] Titanium, [20] and cobalt [21] occupy a unique position in the periodic table due to their distinctive electronic properties, largely attributed to the presence of d-orbital. [22]

II. CHEMISTRY OF TRANSITION METALS CATALYSTS

Transition metals are located in the d-block of the periodic table, signifying that their outermost electrons occupy the d-orbital and have unique properties that set them apart from other elements. Transition metals have partially filled d-orbital that can accept electrons from reactants, facilitating various types of chemical reactions. The geometrical arrangement of these d-orbital can assist in the formation of transition states and intermediates. Transition metals are commonly used as catalysts in various chemical reactions due to their unique properties. Transition metals have the ability to adopt multiple oxidation states. This

flexibility allows them to facilitate oxidation-reduction reactions by providing a platform where reactants can lose or gain electrons, both of which are crucial to their role as catalysts. Transition metals have a high tendency to form coordination complexes with other species. These species can serve as intermediates in a reaction, allowing the reaction to proceed through a more efficient pathway. Transition metals have the ability to adsorb reactants on their surface. This can increase the concentration of the reactants at the catalyst surface and provide a platform where the reaction can occur more efficiently. They can sometimes be toxic, and their use needs to be carefully managed. Many of these catalysts are expensive; so much research is focused on finding cheaper, equally efficient alternative. Transition metals play a significant role in water purification, and facilitate a range of pollution degradation processes.

- 1. Transition Metal Catalysts in Oxidative waste Water Treatment:** Oxidative processes are crucial in waste water treatment to break down pollutants that are otherwise difficult to remove. Transition metal catalysts play a significant role in oxidative wastewater treatment processes, where they are used to facilitate the breakdown and removal of various organic and inorganic pollutants. These catalysts take advantage of the variable oxidation states and unique properties of transition metals to generate highly reactive oxidizing species, such as hydroxyl radicals ($\cdot\text{OH}$) and oxygen radicals ($\text{O}\cdot$, $\text{O}_2^{\cdot-}$), which are capable of oxidizing and degrading a wide range of contaminants.
- 2. The Fenton Process: Iron as a Catalyst:** Fenton's reagent is one of the most well-known oxidative processes used in wastewater treatment. It involves the combination of hydrogen peroxide (H_2O_2) and a transition metal catalyst, typically ferrous iron (Fe^{2+}). The Fe^{2+} ions catalyze the decomposition of hydrogen peroxide into hydroxyl radicals ($\cdot\text{OH}$) through the Fenton reaction. The iron catalyzes the decomposition of hydrogen peroxide into hydroxyl radicals which is powerful oxidant capable of breaking down a wide range of organic compounds. This process is especially effective for treating persistent organic pollutants that are resistant to conventional wastewater treatment methods. [23]



The hydroxyl radicals are highly reactive and can break down various organic pollutants present in the wastewater through a process called advanced oxidation. Fenton's reagent is effective in treating recalcitrant organic compounds that are difficult to degrade by conventional methods.[27] Although Fenton processes are effective for treating stubborn wastewater, it faces challenges including acidic conditions, sludge formation, and high chemical use. However, improvements in a variety of Fenton approaches, particularly in material science and catalysis, provide promise to address these problems. The scalability of advanced Fenton techniques for wastewater treatment hinges on cost, environmental impact, and adaptability. The microbial electrolytic-Fenton cell, which produces H_2O_2 on-site and induces the Fenton reaction with Fe^{2+} , shows promise, especially with optimal voltage, aeration, and Fe^{2+} levels.[28]

When using the Fenton's reaction for wastewater treatment, it's important not only to remove organic materials, but also to reduce the toxicity of the water. Essentially, the success of this method should be measured by how much it reduces toxicity. This approach should be standard for treating all types of hazardous industrial wastewater.[29]The oxidation activity of hydroxyl radicals ($\bullet\text{OH}$) is directly associated with the pH level and functions at a solution pH of 3.

The oxidation potential of the hydroxyl radicals enhances with a decreasing pH value. This is largely due to the scarcity of active Fe^{2+} ions, leading to the creation of inactive iron oxohydroxides and ferric hydroxide precipitates. When the pH values are extremely low, iron complex species such as $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and stable oxonium ions like $[\text{H}_3\text{O}_2]^+$ are present. The existence of these species diminishes the reactivity between Fe^{2+} and H_2O_2 . [30-31]The Fenton process, thus, an oxidation mechanism, operates under various pH conditions and involves several competing reactions.

The reaction rate depends on iron dosage, while mineralization extent is tied to the oxidant concentration. It's crucial to understand the balance of OH production and consumption in the Fenton process. Research has categorized the relationships in the process into three groups, based on the initial ratio of Fe^{2+} to H_2O_2 . [32] However, the Fenton process has limitations, including the high cost of H_2O_2 , substantial ferric sludge production, and increasingly stringent water regulations. Improvements have been sought by introducing energy to enhance OH production, such as in photo-Fenton and electroFenton variants, and by developing iron-based catalysts and reusing Fenton sludge in Fenton-like reactions.

- 3. Photo-Fenton Process:** This is a variation of Fenton's reagent that incorporates the use of UV light. UV radiation enhances the generation of hydroxyl radicals by promoting the photolysis of hydrogen peroxide. The addition of UV light increases the efficiency of the process and allows for the treatment of larger volumes of wastewater. Antibiotics are used a lot and cause big problems in water environments, even in small amounts, because they don't break down easily and can make bacteria resistant to it. [33] Even though a process called homogeneous photo-Fenton is often used to clean up wastewater from medicines, how well it works depends on the balance of certain chemicals and how acidic the water is, all under certain light conditions. [34] All of a certain, antibiotics are quickly removed from water using a specific process, with either iron citrate or iron oxalate. However, when using iron nitrate, it was less effective, only removing a fifth of the antibiotic. This might be due to the fact that iron nitrate used up less hydrogen peroxide than the other two iron compounds did. [35] The process of breaking down a drug called paracetamol works better using iron sulfate compared to potassium ferrioxalate when exposed to sunlight.

This could be because iron sulfate forms more intermediary substances and helps produce more iron. On the other hand, another drug, amoxicillin, was completely broken down using potassium ferrioxalate with just 5 minutes of light exposure, while using iron sulfate took three times as long. [36] Researchers, Kajitvichyanukul and Suntronvipart used this process of photo-Fenton to treat hospital wastewater in a lab setting. By following up with a cheap method called activated sludge treatment, they managed to remove all the pollution as measured by Chemical Oxygen Demand (COD). Even though

other studies show that this photo-Fenton process can break down drugs in the water, it usually needs the water to be at a specific acidity level. So, recently, researchers have started to use a slightly different process that doesn't need the water's acidity to be adjusted. For example, when they treated a compound called kaolinite supported ferrioxalate with a certain amount of phosphoric acid, they were able to remove 99% of amoxicillin from the water in just 10 to 12 minutes without needing to control the acidity of the water. [37-38] A study used a system assisted by ferrioxalate and sunlight to treat wastewater from a drug-making plant on a larger scale. They were able to remove 84% of the pollution measured by Total Organic Carbon (TOC) in less than 2 hours using oxalic acid and iron.

When this system was combined with traditional wastewater treatment methods, it helped to improve the ability to break down the waste. This combination also reduced the cost and time needed for treatment.[39] For instance, a study combined the photo-Fenton process with a biological method (using an Immobilized Biomass Reactor) to break down real wastewater from pharmaceutical production. They found that the level of a stubborn pollutant, nalidixic acid, didn't change after a long time of using the biological method alone. So, they used the photo-Fenton process to help break down this nalidixic acid into substances that are easier to oxidize. They did this by using a certain amount of hydrogen peroxide and it took just over 3 hours to do it. [40] In a different study, they tried to clean synthetic wastewater that contained various pharmaceuticals dissolved in natural water by using a process called nanofiltration. This process was able to decrease the amount of drugs in the water to less than 1.5% of their original amounts. But the photo-Fenton process was able to completely remove the drugs using very less hydrogen peroxide than if it was used singly.

Some studies show that the photo-Fenton process works well to treat wastewater that contains pharmaceuticals, especially when combined with biological methods. This makes it a promising technique to clean the wastewater. The production of food and materials like cotton has always involved using pesticides. These can be herbicides, insecticides, or fungicides, depending on what they're designed to kill. [41-42] In addition to farms, one of the main ways that pesticides get into the environment is from wastewater released by factories that make these pesticides. [43] The pesticides can directly harm the health of living things even in very small amounts; they can be poisonous and can cause diseases. [44] Pesticides are removed from wastewater from factories using physical and chemical methods.

This is because pesticides can be harmful in sudden high amounts and can also harm the microorganisms that are used in some treatment methods. Studies have shown that the photo-Fenton process is effective for breaking down stubborn farm chemicals. It's also been reported as one of the best systems to prepare or treat wastewater compared to other similar methods. For instance, the photo-Fenton process, along with other methods using hydrogen peroxide and UV light, or titanium dioxide and UV light, and also the standard Fenton process, were all tested in a lab to clean up wastewater which contained active ingredients from a fungicide and an insecticide.[45] The results showed that the photo-Fenton process worked better than the other methods at all tested iron and hydrogen peroxide levels. Also, the photo-Fenton process was able to reduce the amount of dissolved organic carbon and chemical oxygen demand in the water to 32% and 27%

respectively in an hour. The standard Fenton process didn't performed well under the same conditions. Methomyl, a very toxic insecticide that dissolves well in water, was also very well treated by this photo-Fenton process.[46] A study was done to see how well the Fenton and photo-Fenton processes could remove this toxic chemical. They found that the photo-Fenton process could completely break down methomyl in half an hour. The standard Fenton process took twice as long and was only able to remove 86.1% of the methomyl. So the photo-Fenton process worked faster and better than the Fenton process. [47] The ability of different pesticides to react to light was ranked; diuron was the most reactive, followed by alachlor, isoproturon, chlorfenvinphos, and atrazine. This order was the same whether the pesticides were mixed together or treated individually. In many cases, it takes a very long time to completely break down pesticide pollution in wastewater. [48]

So, to treat wastewater, it's often a good idea to follow up with a biological treatment process. This comes after the original pesticides have been turned into substances that are less harmful and easier to break down.[49] For example, Farre' et al used a combination of chemical and biological processes to treat wastewater containing two types of herbicides. Among different combinations of Fenton chemicals, they found that certain levels of iron and hydrogen peroxide led to a 31% decrease in Total Organic Carbon (TOC) after 2.5 hours of UV light exposure in the photo-Fenton process. Then, the treated water was put through a secondary biological treatment process for complete TOC removal. After the time period of two days this resulted in a further TOC reduction of up to 87%.

They also used plant-based cleanup technology for treatment of sites polluted with pesticides. [50, 51] However, when there's too much pollution, it can harm the plants used for cleanup. For example, *Solanum nigrum* L. was tested for its ability to clean up a fungicide called metalaxyl from a body of water. But if there's more than a certain amount of this fungicide in the water, it harms the plant. To handle this, the photo-Fenton process was used first to remove the fungicide, and then the plant was used to stabilize the breakdown products and the iron compounds. The plant was able to tolerate a certain amount of iron in the water. [52] The photo-Fenton process is more efficient at removing farm chemicals (more than 60% efficiency) than other similar methods. However, more studies are needed to test how well it works with different mixtures and real industrial waste. Also, we need to study more about how effective it is when used with other treatment processes to get the best results and keep costs down.

- 4. Transition Metal-Catalyzed Ozonation:** Ozone (O_3) is a potent oxidizing agent that is used in wastewater treatment. While ozone isn't a transition metal catalyst, it can be combined with such catalysts like iron or manganese to enhance its effectiveness. These metals can help break down ozone into more reactive oxygen species, like hydroxyl radicals, which further help in the degradation of pollutants. The efficiency of ozone treatment can be improved with higher pH levels, as this raises the production of hydroxyl radicals. The performance can also be boosted by combining ozone with light irradiation, hydrogen peroxide, or catalysts like iron or copper complexes.[53] This process can be complicated due to the different compositions of pollutants in wastewater, making it challenging to determine the ideal ozone dosage for treatment. Certain compounds, particularly unsaturated aromatic and aliphatic ones, are more responsive to

ozone through selective oxidative reactions. [54-55] Studies on ozone's application in wastewater treatment have shown promising results. In a pilot plant, many pharmaceuticals were either fully or partially degraded by ozone. In another study, various pharmaceuticals, including antibiotics and estrogens, were oxidized by more than 90-99% with the use of ozone. This suggests that ozone can be an effective tool for treating many pharmaceuticals found in wastewater. [56-57]

- 5. Transition Metal Catalysts in reductive waste Water Treatment:** Certain transition metals can also catalyze reductive reactions. For instance, zero-valent iron (ZVI) is commonly used for the reduction and removal of several contaminants, including nitrates and heavy metals from wastewater. Reductive processes in wastewater treatment are typically used to handle inorganic contaminants, especially metals and certain forms of nitrogen. Transition metals often serve as catalysts in these processes due to their variable oxidation states and ability to facilitate electron transfer reactions.
- 6. Photo Catalysis with Transition Metal Oxides:** Transition metal oxides, such as titanium dioxide (TiO_2), zinc oxide (ZnO), and tungsten trioxide (WO_3), can act as photocatalysts in the presence of UV or visible light. When irradiated, these catalysts generate electron-hole pairs, leading to the production of reactive oxygen species (ROS), including hydroxyl radicals and superoxide radicals. These ROS can oxidize and degrade organic pollutants and some inorganic contaminants. Certain transition metals, especially their oxide forms e.g., titanium dioxide (TiO_2) and zinc oxide (ZnO), can be used as photocatalysts to treat wastewater under light. When exposed to light (UV), these photocatalysts generate electron-hole pairs. These electron-hole pairs can react with water and oxygen to produce reactive oxygen species (ROS), such as hydroxyl radicals and superoxide anions.

These ROS are highly reactive and can oxidize various pollutants thus degrading them. Metal oxides are substances with unique physical and chemical properties, including strong electron-electron interactions. [58] These properties can be altered through methods such as chemical modification, structural change, doping with different atoms, or creating nano-composites [59]. They are highly stable and can be recycled effectively, making them suitable for a wide range of applications. These include the degradation of heavy metals, detection of poisonous gases, coatings for wearable electronic devices, use in biomedical fields, and breaking down organic contaminants through photocatalysis.

- 7. Titanium Oxide (TiO_2)** Fujishma and Honda were pioneers in exploring the photocatalytic properties of TiO_2 , a widely used material known for its band position, photo stability, electron-shift, charge separation, and non-toxicity. [60] TiO_2 shows superior photocatalytic activity due to its lower photogenerated electron mass, facilitating charge transfer and reducing recombination rate. [61] Despite its wide band gap of 3.0 to 3.2 eV and ability to be synthesized via the hydrothermal method, TiO_2 has limitations. It can only be activated by UV light, using only 4% of solar light, and the anatase phase has poor thermal stability. [62] These limitations can be mitigated by metal doping with elements like Cu [63] Co [64], Mn [65], Fe [66] and Ni [67].

- 8. Zinc Oxide (ZnO):** ZnO is widely studied due to its unique physical and chemical properties, such as its resistance to photochemical corrosion and its enhanced antibacterial activity.[68] It primarily exists in hexagonal wurtzite, cubic zinc-blend, and rocksalt crystal structures with wurtzite being the most stable phase.[69] It has a large band gap of 3.37 eV and a binding energy of 60 meV. Like TiO₂, ZnO has quick photo-induced charge recombination, reducing its photocatalytic efficiency. However, this can be improved by doping or adding materials like TiO₂, [70] Cu₂O, [71] SnO_{2-x}, [72] Ta₃N₅ [73] and graphene oxide. [74]
- 9. Copper Oxide (CuO):** Copper oxide is commonly used in photocatalysis due to its availability, ease of coating, cost-effectiveness, and good photocatalytic activity.[75] Its smaller band gap of 2.17 eV and varying performance based on crystal structures (octahedral and cubes) make it ideal for use as a photoelectrode.[76] In a study, Cu₂O/Cu nanocomposites showed higher photocatalytic activity than Cu₂O in degrading methyl orange.[77] Despite a fast recombination of charge carriers hindering photocatalytic performance, doping and co-doping can solve this issue by shifting the charge carrier interface and broadening the visible light absorption range. For instance, 10% CuO-doped samarium orthoferrite (SmFeO₃) showed improved photocatalytic activity. [78]
- 10. Iron Oxide (Fe₂O₃):** Iron oxide, or Fe₂O₃, has several crystal structures, with α -Fe₂O₃ (hematite) being the most stable, featuring a hexagonal arrangement of iron atoms with six local oxygen atoms. [79] Fe₂O₃, with a narrow band gap of ~2.2 eV, is preferred over materials like TiO₂, Bi₂O₃, ZnO due to its chemical stability, cost-effectiveness, abundance, non-toxicity, and good absorption ability. Its ferromagnetic behavior aids in separating the photocatalyst from the solution after treatment. [80] Despite its drawbacks, such as lower whole diffusion length, high electron recombination rate, and poor conductivity, scientists have developed methods to reduce recombination rate, enhance photocatalytic activity, and improvement upon these limitations. [81]
- 11. Tungsten Trioxide (WO₃):** Tungsten oxide (WO₃) is a cost-effective photocatalytic material with stable physicochemical properties, a small band gap of 2.4-2.8 eV, strong solar spectrum response, exceptional oxidation ability in the valence band, and low toxicity. [82-83] However, its photocatalytic activity is limited due to the low recombination of photoexcited electron-hole pairs and a more positive conduction band. [84-85] Various methods have been used to improve its efficiency, such as morphological control, noble metal deposition, element doping, heterojunction formation, and carbon-based material modifications. [86-88] A significant challenge is the low conduction band edge potential of WO₃, which leads to a higher likelihood of recombination on the surface, making it less effective for full pollutant mineralization.[89] Approaches to address this include widening the band gap and applying an external bias. [90-91]
- 12. Platinum Catalyst:** Platinum is a promising photocatalyst with applications in fields like catalysts, biomedicine, and electronics. However, its high cost poses a barrier to commercialization. [92] Its an efficient co-catalyst due to its ability to quickly trap electrons from the conduction band, which prevents charge carrier recombination and enhances photocatalytic performance.[93] Research has shown that platinum can effectively enhance the absorption of visible light and deliver it to the semiconductor photocatalyst, thus boosting photocatalytic activity.[94]

13. Palladium-Catalyzed Hydrodechlorination: Palladium (Pd) catalysts are often used for hydrodechlorination, a process that can break down chlorinated organic compounds, which are common pollutants in industrial wastewater. The Pd catalyst facilitates the replacement of the chlorine atoms in these compounds with hydrogen, transforming them into less harmful substances. Up to 96% of harmful substances like chlorobenzene have been removed within an hour by using a special type of process involving a metal palladium (Pd) under certain conditions. If a more stable form of palladium is used than this method could be a good way to clean chlorobenzene from water sources. In the future, more research can be done to see how this method can be used in real-life situations, like cleaning up polluted sites. But, there's a potential problem: in real groundwater, there are substances that might make this method less effective. These substances are called radical scavengers, like carbonate, so they need to be studied more. [95]

III. RECOVERY AND REUSE OF CATALYSTS

The practicality of using transition metals as catalysts in wastewater treatment is largely dependent on their recyclability. The recovery of these catalysts from the treated water for reuse can be a complex and costly process. This challenge can be somewhat mitigated by immobilizing the catalyst on a solid support, which can then be separated and reused. However, finding a suitable, durable, and non-toxic support that does not impede the catalytic activity of the metal can be tricky. Catalyst once separated from the reaction mixture can be again recycled many times.

However, for many of the catalytic process the deactivation of catalytic activity is inescapable for various reasons like poisoning, fouling, carbon deposition, thermal degradation, sintering, and leaching of active metal species into liquid phases. [96] At certain point only activity of catalyst which has lost could be regenerated and reused. Thermal calcinations treatment is one of the processes of recovery for removing the unwanted substances present on the surface of the catalyst. [97] However, if still the poisonous substances etc remains on the catalyst and is irreversible, the catalyst become poisonous and cannot be further recycled. This type of catalyst which completely loses its activity and are no more available for reuse and regeneration are called spent. Some of the methodologies of regeneration and reuse are mentioned as follows:

1. Filtration and Centrifugation: It is very traditional method including handling, separation, regeneration and reuse of catalyst metal in laboratory. In filtration commonly the undissolved solids of different sizes are separated from liquids or gas by using a membrane/filter which allows the fluid to pass blocking the solid particles. Mostly this technique, can be carried out through various methods, including gravity filtration, vacuum filtration, and pressure filtration, depending on the specific requirements of the separation process. It is commonly used in laboratories, industries, and even in daily life for tasks such as purifying liquids, separating solids from liquids, and cleaning air or fluids. It's worth noting that while filtration is effective for separating solid particles from a liquid or gas, it may not work as well for separating very fine particles or for mixtures where the differences in particle size are minimal. In such cases, other separation techniques like centrifugation, sedimentation, or chromatography might be more suitable. Centrifugation is a separation technique commonly used to separate heterogeneous

mixtures based on differences in density. It's a powerful method that accelerates the sedimentation process by applying centrifugal force.

This force is much stronger than Earth's gravity and allows for a quicker and more efficient separation of components. Centrifugal force tends the particles to move radially away from the axis of rotation, such that the particles with high density tends particles to be in centre called pellet and particles with less density go towards outward side called supernant liquid. This liquid can be decanted without disturbing the precipitate with Pasteur pipette. [98] A recent work representing the synthesis of substituted amines using Nickel-Copper catalyst has been reported, in which catalyst has been recovered successfully by centrifugation and reused four times. [99]

- 2. Magnetic Separation:** It is a very convenient methodology used for the separation of magnetic catalyst from the solution. It represents an innovative and environmentally friendly approach in chemical processes. This method offers several advantages over traditional separation techniques. [100] The magnetic properties of the solid catalyst allow it to be quickly and efficiently separated from the reaction mixture using an external magnet. This significantly reduces the time required for the separation process compared to other methods.

The process of magnetic separation is relatively simple and convenient. It eliminates the need for complex separation setups and procedures, making it easier to carry out and automate. It can lead to cost savings in the work-up procedure. It reduces the need for additional equipment and steps required for separation, thereby contributing to economic feasibility. Magnetic separation ensures minimal loss of the solid catalyst during the separation process. By minimizing waste generation and energy consumption, magnetic separation contributes to a reduced environmental impact of the overall chemical process.

Overall, the adoption of magnetic separation techniques for solid catalyst separation represents a step towards more sustainable and efficient chemical processes, in line with the principles of green chemistry

- 3. Magnetic Nanoparticles:** Magnetic nanoparticles (MNPs) have garnered significant interest from researchers over the years, primarily because of their versatile applications in creating recyclable catalysts. These nanoparticles can serve as catalysts themselves or act as carriers for catalytic species immobilized on their surfaces. This approach offers a synergy between the benefits of nano-sized particles and magnetic materials. Magnetic nanoparticles (MNPs) often display a fascinating property called superparamagnetism, which is a distinctive type of magnetism observed at the nanoscale.

Superparamagnetism occurs when the size of ferromagnetic or ferrimagnetic nanoparticles becomes very small, typically around 10–20 nanometers. [101] Solution containing magnetic nanoparticles when come in contact of magnets, its magnetic field induces alignment of the magnetic dipoles of the nanoparticles. This alignment follows the direction of the magnetic field lines produced by the permanent magnet. Due to the alignment of the nanoparticles' magnetic dipoles with the magnetic field, the nanoparticles begin to migrate towards the magnet. This migration continues until the

nanoparticles are concentrated at the wall of the beaker that is closest to the magnet. The process of nanoparticles migrating towards the magnet allows the supernatant (the liquid portion of the suspension) to become clear of nanoparticles near the wall opposite the magnet.

This makes it easier to aspirate the supernatant using a syringe, leaving the nanoparticles concentrated at the wall near the magnet. Once the desired separation is achieved, the permanent magnet is removed. Since the magnetic field from the magnet is no longer present, the alignment of the nanoparticles' magnetic dipoles quickly becomes randomized, causing the measured magnetic moment (the overall magnetic property) of the system to decrease rapidly. As a result, the nanoparticles behave as non-magnetic materials. This magnetic supported catalyst can be reused with retaining its initial activity. [102]

IV. CONCLUSION

In summary, while transition metals offer an exciting and promising avenue for wastewater treatment, careful and holistic consideration of these challenges is required to ensure that the solution is effective, economical, and sustainable. With ongoing research and technological advancements, it is hopeful that these challenges can be overcome, paving the way for the widespread application of transition metals in wastewater treatment. This also potential opens a new chapter in our pursuit of more efficient solutions to the global water crisis.

Their unique properties and versatile roles in catalyzing pollutant degradation processes position them as powerful tools for improving wastewater management strategies. Leveraging their multifaceted roles in catalyzing oxidative processes, facilitating harmful nitrate reduction, and participating in advanced procedures like photo-catalysis, transition metals emerge as a significant asset for sustainable wastewater management. However, their deployment needs to be judiciously managed, considering not only their effectiveness and efficiency but also the economic and environmental impact. While the potentials are vast, the application of transition metals also comes with its own set of challenges.

Further research and investment are required to address these hurdles, including technical, economic, and social aspects. In the face of global water crisis, understanding these challenges and finding ways to surmount them will be pivotal to fully harness the benefits of transition metals in wastewater treatment. Moving forward, the future of wastewater treatment lies in the effective and sustainable use of these metals, along with the development of new, green treatment technologies. The implications of such developments will be far-reaching, spanning from public health and agriculture to industry and ecology. As such, continued exploration in this direction stands to bring about significant societal benefits.

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