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Removal of Ni and Cd cations from wastewater using photocatalytic reactions: Review paper

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Abstract

A clean environment and human health depend on removing heavy metal ions from wastewater. Ecosystems and public health are seriously threatened by heavy metal ions, such as nickel (Ni), lead (Pb), cadmium (Cd), vanadium (V), chromium (Cr), and copper (Cu). For example, because of its toxic effects, cadmium is only permitted at 0.005 mg/L in drinking water, while lead has a maximum permissible concentration of 0.015 mg/L. Heavy metal ions have been extracted from various wastewater types using methods such as adsorption, membrane filtration, chemical addition, electrochemical treatment, and photocatalysis. Nevertheless, conventional techniques frequently encounter obstacles like exorbitant operating expenses and restricted effectiveness, with removal rates occasionally falling below 70%. These techniques can also result in hazardous byproducts, which makes wastewater treatment procedures more difficult. Because photocatalysis is so versatile in environmental remediation, it can be used to remove heavy metals. The ability of semiconductor nanostructures based on metal oxides to effectively remove heavy metals from contaminated water has garnered attention recently. For instance, when exposed to particular light wavelengths, zinc oxide (ZnO) and titanium dioxide (TiO2) can remove some heavy metals with up to 95% removal efficiencies. Zeolites have been used increasingly in wastewater treatment over the past 20 years; applications have shown removal capacities of up to 100 mg/g for cadmium and 150 mg/g for lead. This article examines recent developments in using zeolites to extract heavy metals from contaminated solutions. Both traditional and modern wastewater treatment methods are compiled and discussed in this comprehensive analysis, including the application of ZSM-5 zeolites in photocatalytic technology, which can lower operating costs by up to 30% and improve removal efficiencies. Combining zeolites with photocatalytic systems is a viable strategy to raise the efficacy of heavy metal remediation in wastewater treatment.

Keywords: Cadmium; Heavy metal ions; Nickel; Photocatalyst; Wastewater.

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1- Introduction

Modern technology has introduced several heavy metals into the environment, resulting in significant issues [1]. Pollution can alter water's physical, chemical, and biological qualities [2].

Heavy metals in wastewater have increased due to the expansion of industry and human activities. For example, the textile industry, metal smelting, petrochemicals, paper manufacturing, electrolysis applications, the mining industry, the rayon industry, metal rinse processes, and the tanning industry all contribute to this trend. The release of heavy metal-contaminated effluent into the environment threatens the ecosystem and human health. Heavy metals are non-biodegradable and have the potential to cause cancer; therefore, an unreasonable quantity of these metals in water could lead to severe health complications for living organisms. Here are some examples of industrial sources that release heavy metals (HMs) and cause significant water pollution, as shown in Fig. 1. The most prevalent heavy metals found in the wastewater stream include lead (Pb), zinc (Zn), mercury (Hg), nickel (Ni), cadmium (Cd), copper (Cu), chromium (Cr), and arsenic (As). Although these heavy metals can be detected in trace amounts, they are still considered hazardous contaminants. This overview summarizes several heavy metals, including their primary origins, health implications, and the permissible concentration in potable water. The metals above, along with others such as silver (Ag), iron (Fe), manganese (Mn), molybdenum (Mo), boron (B), calcium (Ca), antimony (Sb), and cobalt (Co), are frequently present in wastewater and must be eliminated [4]. Table 1 explains the most common heavy metals, their sources, and toxicity.

The literature has documented various treatment methods for industrial wastewater, including chemical precipitation, ion exchange, electrolysis, membrane filtration, solvent extraction, coagulation-flocculation absorption, and electrochemical processes. However, these methods are not desirable due to their high costs, continuous requirement of chemicals, incomplete removal of certain metals, generation of toxic sludge, and the need for a high level of operational expertise [1].

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Researchers have recently extensively researched various methods to eliminate heavy metal ions. These include electrocoagulation (EC), synthetic and natural adsorbents, magnetic fields, improved oxidation processes, and membranes. These studies examined the merits and drawbacks of a specific technique for treating wastewater, which also involved the elimination of heavy metals. A comprehensive review of the techniques for removing heavy metals from wastewater has not yet been established [4-6].

This review critically and comprehensively examines the available technologies for efficiently removing heavy metal ions from wastewater. Furthermore, selecting the most appropriate method based on removal efficiency, added chemicals or adsorbents, initial concentration, optimal pH value, and other operating conditions is critical.

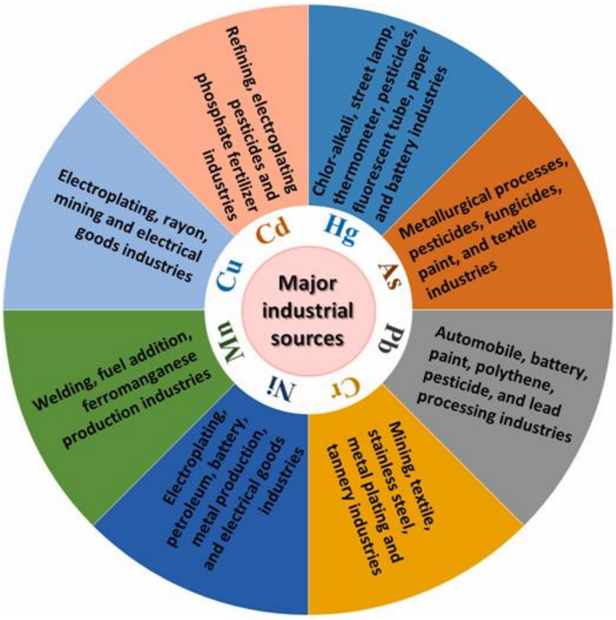

Fig. 1. Major industrial sources of the toxic HM ions [3]

Among these new advanced oxidation technologies, photocatalysis is a popular technology that shows potential in various fields. Fig. 2 depicts the fundamental principle of the photocatalytic process. Generally, semiconductors make up photocatalysts. When light hits a semiconductor, electrons (e^-) in the valence band may jump to the conduction band (CB) and leave a positively charged hole (h^+) on the valence band (VB) if the photon's energy is greater than or equal to the bandgap energy between the VB and the CB. This pair of h^+ and e^- can migrate to the semiconductor's surface to endure a series of oxidation and reduction reactions. The treatment of heavy metals embodies these reactions through the conversion of various valence states. The most important things that slow down the photocatalysis process are the high energy needs of the light that hits them (because of the wide bandgap) and how easily the photogenerated carriers (e^- and h^+) recombine with each other [7].

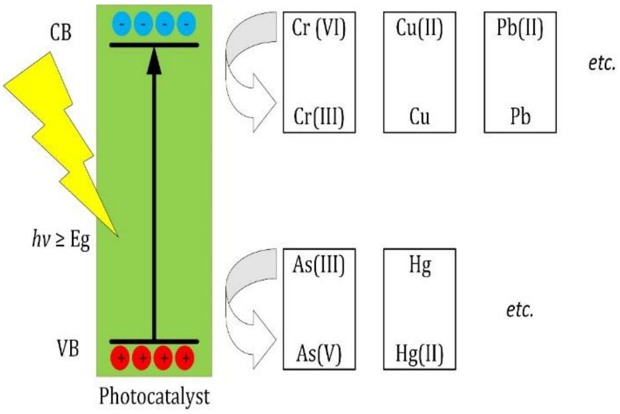

Fig. 2. Schematic diagram of photocatalytic treatment of heavy metals [7]

Heavy metals, including nickel (Ni) and cadmium (Cd), are frequently detected in sewage water due to inefficient waste management, urban runoff, and industrial discharges. There are serious health and environmental dangers associated with their presence in wastewater. Nickel exposure can result in cardiovascular disorders, skin allergies, and respiratory disorders. An elevated risk of lung and nose malignancies is linked to prolonged exposure. Aquatic creatures can bioaccumulate nickel, harming the food chain [8]. In addition to being a human carcinogen, cadmium is highly poisonous and can lead to serious health problems, including kidney impairment and bone fragility. "Itai-Itai" sickness, which is marked by excruciating agony and impairment, can be brought on by prolonged exposure. Plant development and aquatic life are negatively impacted by cadmium, which lingers in the environment and builds up in soil and sediments. Each jurisdiction has different acceptable limits for nickel and cadmium in wastewater. For example, to reduce health hazards, the U.S. Environmental Protection Agency (EPA) advises that cadmium concentrations in effluent should be less than 0.01 mg/L and nickel levels should preferably be less than 0.1 mg/L [8, 9]. Regarding atomic weight, nickel (Ni) has an atomic number of 28 and an atomic weight of around 58.69 g/mol, whereas cadmium (Cd) has an atomic number of 48 and an atomic weight of roughly 112.41 g/mol. Several metals are heavier than cadmium and nickel. With an atomic number of 82 and an atomic weight of around 207.2 g/mol, for instance, lead (Pb) and mercury (Hg) have atomic numbers of 80 and 200.59 g/mol, respectively[8].

Semiconductor oxides for the removal of heavy metal Ions from wastewater TiO_2 is a semiconductor material that is widely employed because of its high abundance, low cost, high stability, low toxicity, and redox potential [10, 11]. The most significant study has been done on TiO_2, the most common photocatalyst. However, it only reacts to UV light due to its large bandgap [12, 13]. As a result, further photocatalysts with appropriate and effective band gaps have been created and put to use, including ZnO [14], C3N4 [15], and Bi-based catalysts [16]. With a band gap of 3.37 eV, zinc oxide (ZnO) is a semiconductor with much interest because of its superior photoelectric qualities and strong chemical stability [3, 17-20]. Unusual electromagnetic characteristics might result from doped ZnO material impurities changing geometrical structures. It is more likely to produce oxygen vacancies and has a cheaper manufacturing cost than TiO_2, which permits a stronger hydroxyl radical generation and a faster reaction. Inappropriate dosages, zinc oxide is both biodegradable and biocompatible. Three crystalline forms of it may be found in nature: salt rock, blende, and wurtzite. The most stable form is wurtzite, a hexagonal cell with lattice parameters of a = 3.2495 Å and c = 5.2069 Å; point group = 6 mm; space group = P63 mc. The rock salt structure forms at high pressures, and blende can only be manufactured on cubic substrates [21].

Table 1. Typical heavy metals existing in wastewater and their sources, in addition to the health issues caused by improper quantities and the permitted amounts in drinking water based on the World Health Organization (WHO) recommendations [22]

Heavy metal	Main sources	Toxicities	Permitted amounts (µg)
Arsenic	Electronics and glass production.	Skin, lungs, brain, kidneys, metabolic system, cardiovascular system, immunological system, and endocrine	10
Cadmium	Batteries, paints, steel industry, plastic industries, metal refineries, and corroded galvanized pipes	Bones, liver, kidneys, lungs, testes, brain, immunological system, and cardiovascular system.	3
Chromium	Steel and pulp mills and tanneries.	Skin, lungs, kidneys, liver, brain, pancreas, tastes, gastrointestinal system, and reproductive system	50
Copper	Corroded plumbing systems, electronic and cables industry.	Liver, brain, kidneys, cornea, gastrointestinal system, lungs, immunological system, and hematological system.	2000
Nikel	Stainless steel and nickel alloy production.	Lung, kidney, gastrointestinal distress, pulmonary fibrosis, and skin.	70
Zinc	Brass coating, rubber products, some cosmetics, and aerosol deodorants.	Stomach cramps, skin irritations, vomiting, nausea, anemia, and convulsions.	3000
Lead	Lead-based batteries, solder, alloys, cable sheathing pigments, rust inhibitors, ammunition, glazes, and plastic stabilizers	Bones, liver, kidneys, brain, lungs, spleen, immunological system, hematological system, cardiovascular system, and reproductive system.	10
Mercury	Electrolytic production of chlorine and caustic soda, runoff from landfills and agriculture, electrical appliances, Industrial and control instruments, laboratory apparatus, and refineries.	Brain, lungs, kidneys, liver, immunological system, cardiovascular system, endocrine, and reproductive system.	6

2- Heavy metals nickel and cadmium

Nickel is primarily used in stainless steel alloys, accounting for 68% of the total nickel used in the modern industrial sector [23]. Other applications include electroplating [24] and the manufacturing of nickel-cadmium batteries and electrical devices [25]. Like other metallic elements, the use of nickel in industrial contexts results in nickel emissions into the surrounding environment. Human activities release more than 20 times more nickel into the atmosphere than is naturally emitted. Collective natural emissions arise from several sources, such as soil particles carried by wind, volcanic particles, fires in forests and plants, and even sea salt sprays. These emissions total around 26,000–30,000 metric tonnes of Ni annually [26]. By 1995, oil combustion to produce electricity and heat emitted the most substantial anthropogenic emissions to the atmosphere, which amounted to 86,000 metric tonnes of nickel annually. Ultimately, soil or aquatic bodies deposit the released nickel into the atmosphere. Furthermore, landfills dispose of 181,000 metric tonnes of nickel, tailings basins dispose of 170,000 metric tonnes, and smelting slag containers dispose of 75,000 metric tonnes. These sources include water, soil, and sediments.

Deficient elevated nickel intake can lead to biological impairment and potentially fatal consequences for species that require it. Exposure to quantities beyond the recommended ideal range can also lead to various forms of biological malfunction and mortality. The specific composition of nickel directly influences its fate and ability to be absorbed by organisms, and consequently, its potential to cause harm to living beings. Nickel carbonyl (Ni (CO_4)) is an example of a substance that easily evaporates and is highly poisonous. The refining process of nickel ore generates nickel during an intermediary phase, intending to create nickel metal. Nickel's behavior in oxygen-deprived water is highly relevant. An example is the appropriate management and containment of radioactive nuclear waste [27]. Because of their technique for absorbing magnesium, aquatic species may inadvertently ingest nickel.

The International Agency for Research on Cancer has classified all nickel compounds as carcinogenic to humans, except for metallic nickel. The precise method by which nickel induces cancer remains unclear [25]. This effect appears to depend on species and tissue. Genetic predispositions may also influence nickel's behavior in a specific organism.

Cadmium, a trace metal frequently found in sediment, facilitates the formation of reactive oxygen species, which are linked to an elevated prevalence of various malignancies.

Elements like arsenic, cadmium, chromium, lead, and mercury have been classified as "heavy metals" due to their elevated atomic weight. These are all-natural substances that are present in varying concentrations throughout the earth's strata. Due to their widespread use, people frequently extract these metals for human consumption. Cadmium is of particular appeal to the industry due to its versatility in various applications, including electroplating and long-life batteries. When used in small quantities, it is beneficial for soil enrichment. Cadmium (Cd^{+2}) is chemically more similar to zinc and mercury than to other transition metals. Due to their mutual affinity, people typically extract it alongside zinc. Mining activities result in the release of previously bioavailable metals and the elevation of various pollutants to the surface, which would have been predominantly inaccessible to groundwater sources. Cadmium is a recognized environmental contaminant that poses a threat to both humans and animals. Miners, construction workers, smelters, and agricultural workers are among the industrial workers at a high risk of direct exposure to trace metals through occupational contact [28].

Smokers are also at a significant risk, as they inhale approximately one microgram per cigarette. This is partially attributable to the tobacco plant's propensity to accumulate cadmium in the soil [29]. Despite this utilization, food continues to be the predominant source of human contact with metals. The risk of Cadmium exposure is elevated due to the high soil content and the presence of cadmium in industrial residue and pesticides. Cadmium's abundance in the soil makes it accessible for crop assimilation, particularly in cereal grains and leafy vegetables. According to the most recent estimates, humans' daily intake of Cadamium ranges from 8 to 25 micrograms [30].

The Food and Agriculture Organization of the United Nations/World Health Organization Expert Committee on Food Additives and Contaminants (JECFA) has established a provisional weekly tolerable intake (PTWI) of 5.8 µg/kg body weight. However, more recent studies conducted by the European Food Safety Authority (EFSA) and the US Agency for the Toxic Substances and Disease Registry (ATSDR) have reduced this estimate to approximately 2.5 g/kg [31].

3- Removal methods of heavy metals

Reverse osmosis, ion exchange, advanced oxidation processes, and absorption are techniques used to filter organic chemicals from wastewater. However, they are unfavorable due to their significant investment requirements and high running costs [32]. Conversely, surface adsorption is easy to understand, manageable, and economically viable [33]. It is a highly effective process that can potentially purify and remove organic matter [34]. Cadmium and nickel, typically present in chemical and petrochemical effluents, are toxic and pose health hazards. Numerous investigations have been conducted to identify more efficient methods for removing nickel and cadmium. Researchers have investigated various treatment methods, including biological treatment, chemical oxidation, air removal, and absorption to eliminate cadmium and nickel from effluent. According to these studies, adsorption is the most effective treatment method because it allows for the recovery of the adsorbent [35-38]. Researchers have studied the adsorption behavior of cadmium and nickel using a variety of materials and purification techniques. These materials include resins [39] , surfactant-modified zeolites [40], organoclay [41], carbon nanotubes [42], and organo-clay.

3.1. Advanced oxidation

When extremely reactive hydroxyl radicals (OH-) or reactive oxygen species (ROS) are produced, new technologies, like advanced oxidation processes (AOPs), offer chemical treatment methods that might work much better than traditional methods. The transfer of one or more electrons from an electron donor (regenerator) to an electron acceptor (oxidant) is the definition of oxidation. Electron transfer occurs when an oxidant and a reducing agent are chemically transformed, resulting in the formation of radicals, which are highly reactive and unstable. Fluorine, chlorine, hydroxyl radicals, and ozone are the most potent oxidants. Although these oxidants can disinfect, they are subject to certain constraints. For instance, ozonation can also result in the formation of DBPs, such as bromate, which has a limited expiration life [43, 44]. Hydrogen peroxide, an additional oxidant, is a disinfectant significantly less effective than ozone or chlorine, rendering it a less desirable alternative [45]. One category of AOPs that has been shown to improve disinfection capabilities is light-activated processes. In light-activated processes, the interaction of photons with a catalyst triggers the formation of free radicals. Since 1988, researchers have documented the disinfectant properties of titanium dioxide (TiO2), a photocatalyst frequently used in this process [46].

3.1.1. Photocatalyst

Since the discovery of photocatalytic water splitting in 1972 by Fujishima and Honda, much research has been conducted to investigate TiO_2 materials [47]. Photocatalysis represents a technologically auspicious resolution for many synthetic precursors and products utilized in producing fine chemicals and fuels [48]. Photocatalysis is the process of a photoreaction occurring in the presence of a catalyst. This process may be categorized into homogeneous and heterogeneous photocatalysis [49]. The reactants and catalysts are present in the same phase during homogeneous photocatalysis. Ozone and the photo-Fenton system are typical photocatalysts. The OH ion is the active species and is used in several ways. There are two phases in the ozone's synthesis of •OH.

$$\bullet OH^{+} \bullet OH \rightarrow H_2O_2 + hv \tag{1}$$

The following procedure is how the Fenton system generates hydroxyl radicals.

$$Fe^{2+} + HO\bullet \rightarrow Fe^{3+} + OH^{-} \tag{2}$$

This approach harnesses sunlight with a wavelength of 450 nm, hence circumventing expensive energy methods.

The drawback of this approach lies in the need for low pH levels during the process [50]. Heterogeneous photocatalysis emerged as a novel Advanced Oxidation Process (AOP) near the end of the 20th century, with over 2000 articles dedicated to the topic. Currently, about 1000 papers are published annually. Heterogeneous photocatalysis has high efficiency in green chemistry, fine chemicals, and developing advanced oxidation processes (AOP). Currently, there is a preference for studying this particular field. However, it is essential to remember that photocatalysis can provide specific and gentle oxidation for organic fine chemistry [51]. Fig. 3 shows the applications of photocatalysts.

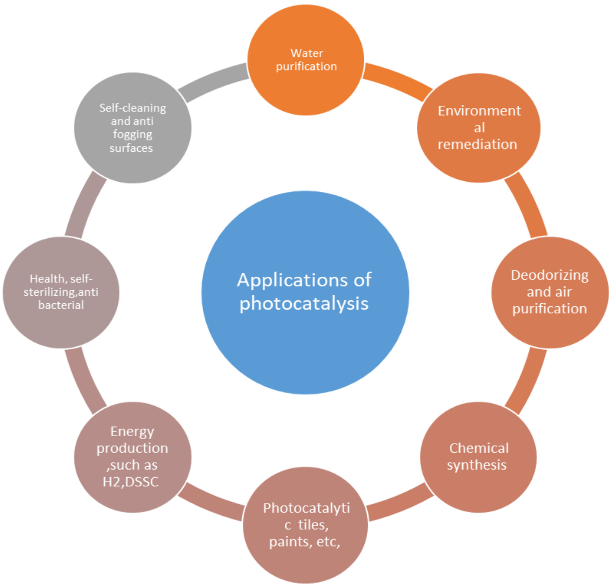

Fig. 3. Applications of photocatalysts

Photocatalysis is a subfield of chemistry that focuses on chemical processes that occur in the presence of both light and a photocatalyst. A photocatalyst is a type of semiconductor that increases the speed of the chemical process. Photocatalysis has many uses, such as antimicrobial, deodorizing, air purification, antifogging, self-cleaning, and water purification. Superhydrophilicity is a critical phenomenon in some applications. Photocatalysis is an environmentally friendly chemical process that is now essential. The following Table 2 indicates a group of photocatalysts used to remove heavy metals. Water is a requirement for humans, animals, and plants. Due to the continuously growing population, the water demand is steadily rising, and thus, there is a necessity to cleanse water in Fig. 4.

3.1.2. Photocatalysis mechanism

Heterogeneous photocatalysis, which utilizes semiconductor materials, typically involves a radio wire that gathers light and a few microorganisms that circulate to aid in the breakdown of contamination. An information light with an ultra-band-hole vitality (hn > Eg) shines on the semiconductor. This causes a VB electron (e^-) to be excited by the CB, which leads to the loss of a photogenerated opening (h^+) at the VB. The electron-hole pair then engages in a redox reaction and relocates to the material's surface. Three primary species participate in a photocatalytic reaction: a hydroxyl radical, a superoxide radical, and a hole that generates hydroxide radicals as a preliminary oxidant. Typically, researchers use two courses to determine the age of OH radicals.

- Hole oxidized H_2O and OH^- radical to form OH radical in an aquatic environment.
- Oxygen exhibited in the watery arrangement decreased electrons to form oxide radicals.

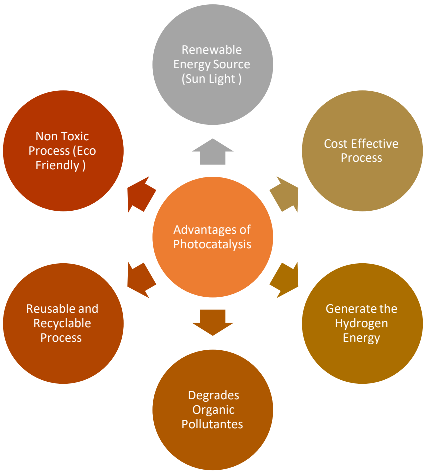

Fig. 4. Advantages of Photocatalysis.

The photogenerated h^+ is generally considered an oxidant designed to degrade natural defiles. The impetus composition and oxidation conditions determine the limit of this effect [64]. Fig. 5 provides a concise explanation of each of these stages. It is important to note that the electron actuated by a photograph can easily recombine with h^+ after reaching an advanced age, without using electron or gap scavengers. In this way, the proximity of specific scroungers is essential for enhancing the efficacy of photocatalysis and suppressing charge recombination rates. We must meet fundamental requirements to design a photocatalyst that effectively utilizes sustainable and renewable solar energy. First and foremost, the semiconductor material should have a smaller band gap to facilitate the retention of solar energy over a wide range of wavelengths. At the same time, the semiconductor needs to have a moderately positive valence band so that h^+ and OH radicals can be made in large amounts. Secondly, the impetus should have a specific stage or framework for productive charge partition and transportation [65, 66]. Additionally, the semiconductor materials should exhibit exceptional photoelectrochemical stability in their electrochemical responses [67]. In addition to the electron band structures, other factors, such as material selection, morphological engineering, crystallinity, and surface properties, are essential when developing a stable and effective photocatalytic system that is light-responsive [68]. The choice of semiconductor materials is particularly critical, as it determines the degree of visible light reaction and, consequently, the overall efficacy. The privileged morphological design, which briefly separates the photograph-bearing intersection and the redox response focus, can improve the transporter detachment and transportation [69]. Additionally, a high level of crystallinity with precious stone deformities would enhance the efficiency of the photogenerated electrons and gaps to participate in the desired responses, thereby limiting interface recombination [70]. The photocatalytic action is also significantly influenced by the surface terrain of the photocatalysts, which is dependent on the porosity and geometrical condition of the materials. We infer this from the fact that the adsorption of contaminants represents a fundamental advancement [71].

Table 2. Overview of the types of photocatalysts used in heavy metal removal

Photocatalyst	**Heavy Metal**	**Light Type**	**Irradiation Time**	**Efficiency**	**References**
TiO2	Cr(VI)	Visible light	80 min	100% (formic acid as electron donor)	[52]
TiO2 hollow sphere	Cr(VI)	UV light	80 min	0.0867 min^{-1}	[53]
Ag/TiO2	Cd(II), Ni(II), Zn(II), Mn(II) and Cu(II)	UV light	120 min	100, 96, 65.13, 58.22 and 56.20%	[54]
TiO2 nanotube arrays/Ag-AgBr	Cr(VI)	Solar light	180 min	58.63%	[55]
CdS/TiO_2	Cr(VI)	Visible light	180 min	$2.14 \times 10^{-2} min^{-1}$	[56]
ZrO_2	Cr(VI)	UV light	90 min	About 100%	[57]
$ZnTiO_3/Zn_2Ti_3O_8/ZnO$	Cr(VI)	Full-spectrum light	150 min	47%	[58]
ZnO–graphene	Cr(VI)	UV light	240 min	98%	[59]
Nb_2O_5	Cr(VI)	Full-spectrum light	١٢0 min	90%	[60]
Chitosan/Ag	Cu(II), Pb(II) and Cd(II)	Natural sunlight	240 min	1.10×10^{-4}, 1.4×10^{-4} and 1.5×10^{-4} mol dm−3s^{-1}	[61]
SnO_2 nanoparticles	Co(II)	UV light	60 min	94%	[62]
Porous BNNSs/TiO_2	Cr(VI)	Simulated solar light and visible light	70 min and 80 min	99%	[63]

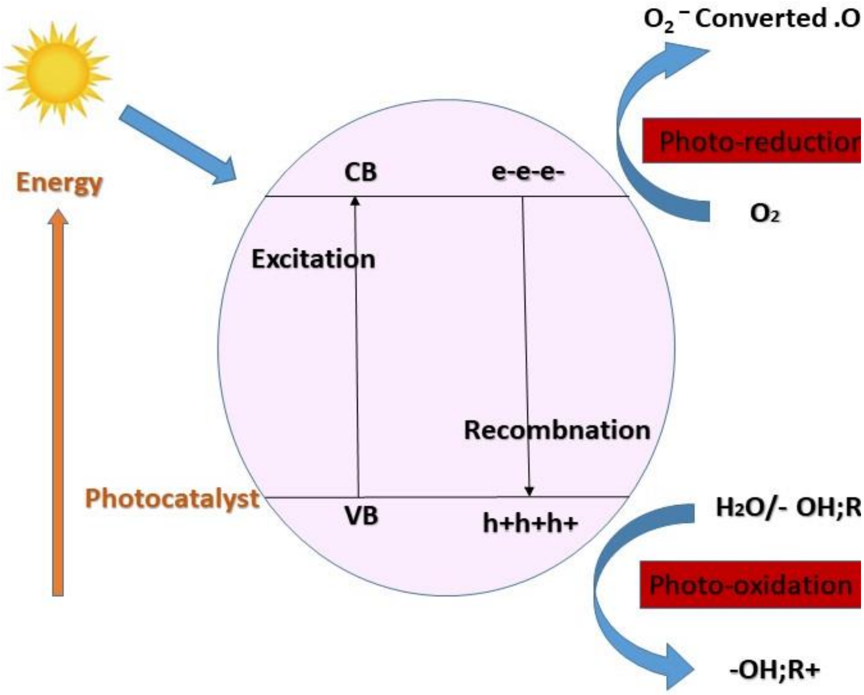

Fig. 5. Mechanism of photocatalysis [72]

3.2. Heterogeneous photocatalysts

Two photons (light) and an impetus (semiconductor) are required to initiate the substance response, which is why photocatalysis combines two primary subjects: photochemistry and catalysis. UV (300–388 nm) or unmistakable (388–520 nm) light sources can generate photons depending on the semiconductor materials used. The semiconductor materials are characterized by a vacant CB (Conduction band) and VB (Valence band). A photon with enough energy, which is the same as or higher than the band gap energy (Eg), can move the electron from the VB to the CB as shown in Fig. 6 Upon excitation, the electron moves from the valence band to the conduction band, leaving a positive charge in the VB, known as a gap (h^+). We commonly refer to this as charge detachment, marking the beginning of a photocatalytic response. The photogenerated electron-opening sets can be associated with a few conceivable responses.

- The information vitality is dispersed as heat resulting from the recombination of electrons and gaps.
- The metastable state captures electrons and holes.
- Interaction with electrons or holes on the surface or within a semiconducting material

An ordinary photocatalytic process can be represented as a four-stage framework in which an electronic stage is associated with a light source in addition to the fluid (watery, naturally dissolvable), strong (photocatalyst), and porous stages (oxygen, nitrogen). The initial step in a photocatalytic response is the development of electron-gap sets, followed by oxidation and/or reduction reactions [74, 75]. Despite being within the sight of an opening scavenger, the oxidation responses become substantial in the presence of an electron forager (oxygen). Environmental science and research in environmental pollution (formic corrosive, methanol, and so forth) can circumvent the oxidation response, and the decreased response transitions into the guideline response.

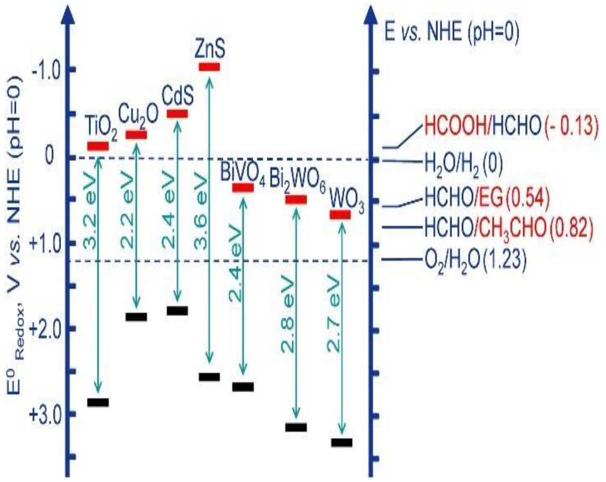

Fig. 6. Energy band gaps of different materials vs. NHE [76]

4- Catalysts used in heavy metal removal

One promising approach for oxidizing or reducing hazardous contaminants is photocatalysis. Heterogeneous photocatalysis is emerging as an innovative technique for removing and restoring heavy metals. This method enhances the processes of detoxifying wastewater pollution by generating electron-hole pairs in semiconductors. The primary objective of this section is to delve deeper into the thermodynamics, energy dynamics, and other intricate aspects of the photocatalytic reduction of metal particles (or metalloids) in light of recent advancements in photoreactors and photocatalysts [75]. TiO_2 and ZnO were selected as photocatalysts for the experiments because they are water-insoluble, photostable, non-toxic, cost-effective, and demonstrate higher photocatalytic efficiency. In recent years, titanium dioxide (TiO2) nanoparticles have gained significant attention due to their unique properties and potential applications in various fields, such as photocatalysis, solar energy conversion, environmental remediation, and sensor technologies [76]. Several techniques are currently employed to synthesize TiO_2 nanoparticles, including sol-gel synthesis, hydrothermal methods, chemical vapor deposition, and flame synthesis. Among these, chemical methods, especially the sol-gel process, stand out for their ability to produce TiO_2 nanoparticles with precise control over size, morphology, and crystallinity.

The product's exceptional purity, the narrow range of particle sizes, and the production of a consistent nanostructure at low temperatures are the sol-gel technique's primary benefits. Metal nano oxides are often synthesized using this technique [77]. Since TiO_2 has a greater specific area, a more negative conduction band edge potential (higher potential energy of photogenerated electrons), is non-toxic, photochemically stable, and reasonably priced, it is often favored in anatase form due to its vigorous photocatalytic activity [78]. ZnO nanoparticles are now created using a variety of processes, such as sol-gel synthesis, physical vapor deposition, hydrothermal/solvothermal procedures, microemulsion methods, and precipitation. Chemical synthesis is an essential process that uses several precursors and specific parameters, including temperature, time, and reactant concentration [79].

The primary benefit of chemical processes is their capacity to generate particles with particular sizes, compositions, and structures. These particles can be used in electrical devices, sensing, and catalysis, among other areas. Additionally, some chemical processes—especially the sol-gel approach—require less energy and lower processing temperatures for synthesis, making them more economical than physical methods [80]. The sol-gel procedure allows for exact control over the chemical makeup and homogeneity of the final nanoparticles by converting a system from a liquid "sol" into a solid "gel" phase. This procedure effectively creates ZnO nanoparticles since it can be scaled up and processed at low temperatures.

The presence of heavy metals in effluent—such as nickel (Ni), lead (Pb), cadmium (Cd), vanadium (V), chromium (Cr), and copper (Cu)—poses a significant environmental concern. For many years, these inorganic pollutants have been non-biodegradable, leading to the accumulation of their harmful effects. In recent years, semiconductor nanomaterials derived from metal oxides have emerged as effective solutions for removing heavy metals from contaminated water through photocatalytic ion reduction when exposed to specific wavelengths of light. Titanium dioxide (TiO_2), zinc oxide (ZnO), and binary nanomaterials combining both types of oxides are among the most commonly used semiconductor oxides for these applications [80].

The study examined the use of illuminated TiO_2 to remove Cr (VI) and Ni (II) through photocatalysis. The experimental setup involved varying the pH of the solution, the duration of contact, the dosage of TiO_2, and the initial concentrations of Cr (VI) and Ni (II). The photocatalytic process effectively led to the near-complete removal of both contaminants, as Cr (VI) and Ni(II) were adsorbed onto the surface of TiO2 and subsequently reduced to Cr(III) and Ni(0). This reduction technique was recognized as a highly effective method for eliminating Cr (VI) and Ni (II) from wastewater. Interestingly, as the pH increased, the removal efficiency of Cr (VI) decreased, while the removal of Ni (II) improved. The dosage of TiO_2 also played a crucial role in the elimination of Cr (VI), with a 1 g/L TiO_2 dose resulting in a consistent enhancement in the removal rates of both Cr (VI) and Ni (II) [81].

Another study evaluated the effectiveness of photocatalytic processes in removing cadmium (Cd^{2+}) and lead (Pb^{2+}) in both continuous and batch systems. The research utilized reactors comprising three components: an ultraviolet (UV) radiation source, an electrochemical cell, and a blending enclosure. Experiments were conducted with both a batch reactor and a continuous reactor to treat synthetic wastewater, maintaining Cd^{2+} and Pb^{2+} concentrations at a constant 25 mg/L throughout the study.

The impact of titanium dioxide (TiO_2) dosage, pH levels, and air dispersion on the efficacy of Pb^{2+} removal was thoroughly examined. The results indicated that increased TiO_2 dosage and pH levels correlated with higher cadmium and lead removal rates. Specifically, the optimum results were achieved at a TiO_2 dosage of 0.9 g/L and a pH of 11, yielding removal rates of 99.8% for cadmium and 99.2% for lead. Additionally, increased air dispersion led to enhanced removal efficiency, with the maximum observed at an air dispersion rate of 2 cm^3/L, resulting in removal efficiencies of 88% for Cd^{2+} and 93.2% for Pb^{2+} over a contact duration of 56 minutes.

The photocatalytic process is an advanced oxidation process (AOP), which is significant because it is cost-effective in eliminating organic pollutants. Titanium dioxide (TiO_2) is an affordable substance that cannot dissolve in water, is not harmful, and exhibits high reactivity [82]. The TiO_2 photocatalytic method was tested to see how well it could remove lead (II) and cadmium (II) from industrial wastewater.

Adsorbate efficacy may decrease at low pH due to protonation and competition between protons and metal ions for adsorption sites on the sorbent [83]. Zeolite is recognized as one of the most effective methods for removing pollutants from water and wastewater. Although zeolite possesses distinctive photophysical properties—such as high-capacity adsorption, numerous microcavities, and chemical-thermal stability—its use has certain limitations. Therefore, enhancing the pollutant removal capacity of zeolite particles through the deposition of photocatalysts has garnered significant interest. In this study, fine zeolite particles were coated with TiO_2 nanoparticles.

The investigation successfully deposited TiO_2 nanoparticles onto natural zeolite, and the resulting composites were characterized using XRD, SEM, BET, and DRS analyses. The incorporation of TiO_2 nanoparticles caused a redshift in the absorption edge and reduced the bandgap energy, although it also decreased the specific surface area. The photocatalytic properties of the composites were assessed under UV light radiation by measuring the efficiency of methylene orange (MeO) and cyanide ion removal, as well as hydrogen production from water and methanol. The findings indicated that optimal photocatalytic performance is achieved by adding an optimal amount of TiO_2 to the zeolite particles (10% wt.). The photocatalytic effectiveness of the ZT composites surpassed that of zeolite or TiO2 alone, attributable to the formation of electron-hole pairs in TiO_2 and the role of zeolite in diminishing the electron-hole recombination rate, which contributes to a greater specific surface area [84].

The textile industry's expanding development has the potential to harm the environment, as it produces dye wastewater that is difficult to eradicate, in addition to providing economic benefits. Procion red is a synthetic textile pigment toxic to aquatic environments and requires proper processing. The most effective method of purifying dye wastewater is the photocatalytic method, which can remove the hazardous pollutants in the wastewater. To produce and characterize the ZnO-Zeolite nanocomposites for photocatalytic applications, which were tested with a 50 mg/L procion red dye sample. The ZnO-Zeolite nanocomposites demonstrate the highest degradation percentage compared to synthetic zeolites or ZnO alone.

The ZnO-Zeolite nanocomposites rely on zeolite adsorbents to absorb dyes and photocatalysts to facilitate the dye degradation. When exposed to a UV lamp, ZnO in nanocomposites will enhance the dye's degradability. A photocatalytic method will increase the percentage of dye degradation with ultraviolet light. This method will degrade the hazardous components of the dye and generate a safer final waste [85]. The photocatalytic method creates hydroxyl radicals that serve as potent oxidizers during the waste degradation. This process is both straightforward and expeditious. Combining the ZnO photocatalyst and synthetic zeolite adsorbent maximizes pollutant degradation results and enhances photocatalysis effectiveness. The formation of hydroxyl radicals as an oxidizer of organic pollutants is a common chemical feature in the photocatalytic process [86].

The nanocomposites were composed of synthetic zeolite adsorbents and ZnO semiconductors prepared using the sol-gel method. The ZnO-Zeolite nanocomposite's surface area value increased to 95.98 m^2/g, its pore size was 4.42 nm, and its total pore volume was 0.08 cm^3/g. The average crystalline size of the ZnO-Zeolite nanocomposite was 32.87 nm. The ZnO-Zeolite nanocomposite has achieved a 90.42% dye degradation rate after 120 minutes [85].

The photodegradation method is both cost-effective and straightforward to implement [87]. Photocatalysis is a combination of photochemical processes and catalysts. The photocatalytic process commences with forming pairs of positive electron holes (e, h^+) in semiconductor particles.

5- Advantages and limitations of heavy metal removal methods

While all heavy metal wastewater treatment techniques can potentially eliminate heavy metals, each has inherent advantages and constraints.

Adsorption is a widely accepted technique for removing heavy metals from low-concentration effluents containing heavy metals. The exorbitant cost of AC restricts its utilization in adsorption. Researchers have developed and evaluated numerous low-cost adsorbents to remove heavy metal ions. Nevertheless, the efficacy of adsorption is contingent upon the nature of the adsorbents. The biosorption of heavy metals from aqueous solutions is a relatively new process with great potential for removing heavy metals from effluent.

Increasing the surface area and pore size of activated carbon can enhance its effectiveness—several studies employed activated carbon to eliminate heavy metals from wastewater. The scarcity of commercial activated carbon (AC) leads to a rise in its cost. Activated carbon is highly advantageous for wastewater treatment due to its large surface area, significant porosity, and flexibility. Carbonaceous sources like biomass, lignite, and coal typically serve as the source of carbon adsorbents. However, the manufacturing of activated carbon primarily uses coal, Biosorbents are regarded as a cost-effective adsorbent that is practical and may be acquired from numerous industries as a byproduct. The key variables that influence the efficacy of biomass in the adsorption process are pH, temperature, adsorbent dose, metal concentration, and contact duration [2].

Due to their straightforwardness and cost-effectiveness, chemical-based separations have been extensively utilized to remove heavy metals. However, chemicals must be used to adjust pH levels and enhance ion buildup. The process generates a substantial amount of sludge, necessitating further treatment. The electrochemical treatment offers rapid treatment, precise control, simplified sludge removal, and reduced chemical usage. Nevertheless, this approach's primary obstacles include the exorbitant expense of anodes and cathodes, limited production capacity, and excessive energy consumption. Utilizing renewable energy sources to drive the coupling between various electrochemical treatment techniques shows promise for resolving this limitation. The most suitable options for combining with other technologies to remove organic and inorganic pollutants from wastewater are aerated EC and electrochemical oxidation procedures. The flotation technique produces less sediment. As a result, this technology is ideal for integrating into constructing an effective and economical electrochemical treatment system [3].

Ion exchange has been widely applied to remove heavy metals from wastewater: efficient elimination, rapid kinetics, and extensive treatment capacity. However, chemical reagents must regenerate ion-exchange resins when exhausted, and the regeneration can cause severe secondary pollution. Also, it is expensive, especially when treating a large amount of wastewater containing heavy metals in low concentration, so it cannot be used on a large scale.

Chitosan (CS) is a naturally occurring polymer with adsorptive properties. It effectively removes contaminants from wastewater because it contains amino (-NH_2) and hydroxyl (-OH) groups. Despite its distinctive characteristics, inadequate mechanical strength and limited stability hinder its effectiveness, leading to ineffective regeneration. Furthermore, using CS in its powdered or flake state is difficult due to its limited permeability, small surface area, hindered mass transfer, and elevated crystalline structure [60, 61].

Mineral adsorbents, such as zeolite, silica, and clay, are highly regarded as effective options for water filtration due to their low operational expenses. Clay has exceptional cation exchange capacity (CEC), cation exchange selectivity, hydrophilic surface properties, a high capacity for swelling and expanding, and surface electronegativity. Furthermore, the use of acid washing, heat treatment, and pillar-bearing techniques may effectively enhance the dimensions of the pore size, pore volume, and specific surface area.

As a result, there is a significant increase in adsorption efficiency [66, 77]. The magnetic field, surface charge, and characteristics associated with redox activity influence the adsorption process. They demonstrated a cost-effective, straightforward synthesis, exceptional surface charge, and the potential for reuse [68]. Although MOFs possess impressive characteristics and are effective in extracting heavy metal ions, they have micropores that are not accessible to some specific metals. Additionally, the majority of them have poor water stability. Metal-organic frameworks (MOFs) have utilized manganese (Mn), iron (Fe), and copper (Cu). However, most of these MOFs have exhibited inadequate chemical stability [3].

Membrane techniques are critical in wastewater treatment and have emerged as a highly favorable choice. They are already very suitable for specific separation applications, including desalination. Membrane processes exhibit a notable capacity for extracting metal ions with high efficiency.

Nevertheless, this approach is hindered by issues such as membrane fouling and biofouling, poor recovery efficiency for the volume of feed wastewater, process complexity, the need for pre-treatment, frequent membrane cleaning, and high cost. To improve the effectiveness of industrial wastewater treatment, it is necessary to create new membrane materials that have improved thermal and chemical stability. These materials should also possess greater anti-fouling capabilities and higher selectivity for the target metals. Both adsorption and membrane technologies in industrial facilities require additional implementation and development to achieve autonomous operation [3].

When coagulation-flocculation is used to treat heavy metal effluent, the sludge that is made settles down and loses water more quickly. However, this approach necessitates the production of a greater volume of sediment and the consumption of chemicals. Coagulation and flocculation are not fully effective in treating heavy metal wastewater. Consequently, coagulation and flocculation necessitate the use of additional treatment methods. Utilized precipitation, coagulation, and flocculation techniques employing ferric chloride to eliminate tungsten from industrial effluent. The most effective method for removing tungsten was discovered under acidic circumstances, namely with a pH below 6, achieving an efficiency rate of 98–99%. We investigated the spontaneous reduction-coagulation process by utilizing a micro-alloyed aluminum composite in a laboratory semi-flow system to treat simulated heavy metal wastewater. After just 20 minutes of treatment, the remaining concentrations of metals were under acceptable limits [84].

The photocatalytic technology has excellent redox capability, adaptability, and performance in the remediation of organic contaminants in water. This makes it easier to utilize for the recovery of heavy metals. Its primary benefit is that it does not necessitate any energy input beyond light energy, distinguishing it from numerous conventional processes and facilitating its continuous operation. Photocatalytic redox does not generate any polluting intermediates. This is an additional significant benefit. This environmentally beneficial feature follows the objective of water remediation. Lastly, photoreactions can be implemented to deposit heavy metals readily reduced on the catalyst's surface in particulates, thereby achieving the effect of direct separation from the solution. Many conventional heavy metal processing methods lack these photocatalytic characteristics.

Even though all of the techniques above can be implemented to treat heavy metal wastewater, it is crucial to note that the selection of the most appropriate treatment technique is contingent upon the initial metal concentration, the component of the wastewater, capital investment, operational cost, plant flexibility and reliability, and environmental impact [87].

6- Zeolites: Structure, classification, and properties

Silicon, aluminum, and oxygen elements synthesize or form aluminosilicates, which are zeolites. The charge-balancing non-framework cation M has valence n, x is two or more, and y is the number of water molecules in the cavities. Its chemical formula is M_2/n O. Al_2O_3.x SiO_2.y H_2O. Shared oxygen molecules connect the Al and Si tetrahedral atoms, or T-atoms, to form a three-dimensional (3D) framework of AlO_4 and SiO_4 tetrahedral. While the SiO_4 tetrahedral maintains charge balance, a positive charge on M counterbalances the negative charge of the AlO_4 tetrahedral. Furthermore, it demonstrates the compositional ranges of significant zeolites [88].

The zeolite framework is composed of interconnected cavities and channels that are inhabited by water molecules and cations. Generally, the cations are mobile and can be exchanged with other cations, thereby changing the pore diameter. Sometimes, we can reversibly eliminate intercrystalline water [89].

The catalytic activity of zeolite is attributed to acidic sites, which are electron acceptors identified as Lewis centers (L) and proton donors accepted as Bronsted (B) sites. Zeolites contain both Lewis acid sites and Bronsted acid sites. While the latter can be charge-compensating cations or trigonal aluminum atoms at cation positions or in oxygen-deficient sizes, the former are protons affixed to lattice oxygen atoms [90].

The precise sequence in which a network of tetrahedral units connects determines the crystal structure of a zeolite. Four- and six-membered rings unite to form a cubic octahedron, sodalite unit in A, X, and Y zeolites. The oxygen bridges between the six-membered rings form the hexagonal prism (zeolite X and Y), connecting these sodalite units. The framework cages leave 8 (zeolite A) or 12 (zeolite X, Y) oxygen-membered apertures, responsible for the pore structure. The arrangements are as follows: in the Mordenite framework, TO4, the tetrahedral is arranged to form five-membered rings, which then join to form five chains. Then link the chains to form the crystal [91].

Another classification of zeolites is contingent upon the pore dimensionalities, which vary among the various types of zeolites. Zeolite may possess pore structures that are one, two, or three-dimensional. Type A's structure is characterized by three intersection channels, whereas ZSM-5 has two intersecting channels—one linear and the other sinusoidal. Mordenite, on the other hand, has a single-channel system that resembles a bundle of soda straws [92, 93]. Fig. 7 and Fig. 8 illustrate an example of pore structure for different types of zeolites [88].

ZSM-5 selectively adsorbs organic molecules in the presence of water, whereas aluminosilicate zeolites are hydrophilic. This is due to its hydrophobic and organophilic character [94].

The framework of ZSM-5 comprises eight-membered rings and features a novel configuration of linked tetrahedral, as illustrated in Fig. 9 A.

As shown in Fig. 9 B, joining these ZSM-5 units through the edge forms the chain. You can connect the chain to form sheets, and the coupling of sheets creates a three-dimensional framework structure. A parallel, straight channel goes in the same direction as the arrow (010) and has an elliptical cross-section of 5.1 x 5.8 Å. There is also a second system of sinusoidal, or zigzag, channels that run perpendicular to the straight channels and have a nearly circular cross-section of 5.4 x 5.6 Å, as shown in Fig. 9 C [95].

The ten-membered rings of oxygen atoms generate two distinct channels: straight (elliptical) and sinusoidal (circular). Channels' effective diameter is intermediate between small-pore zeolite (type A and erionite zeolite) and large-pore zeolite (faujasite and mordenite). ZSM-5 crystallizes in the idealized or rhombic system with lattice constants a = 20.1, b = 19.9, and c = 13.4, as illustrated in Fig. 10 [95].

The mole ratio of oxides can be used to ascertain the composition of ZSM-5.M is a mix of a tetra-alkyl-ammonium cation (with 2–5 carbon atoms preferably) and an alkali metal cation, especially sodium. The mixture is made up of: 0.9 ± 0.2 $M_{2/n}$ O: Al_2O_3: 5 − 100 SiO_2: Z H_2, Z ranges from 0 to 40, and n indicates the valence of the cation.

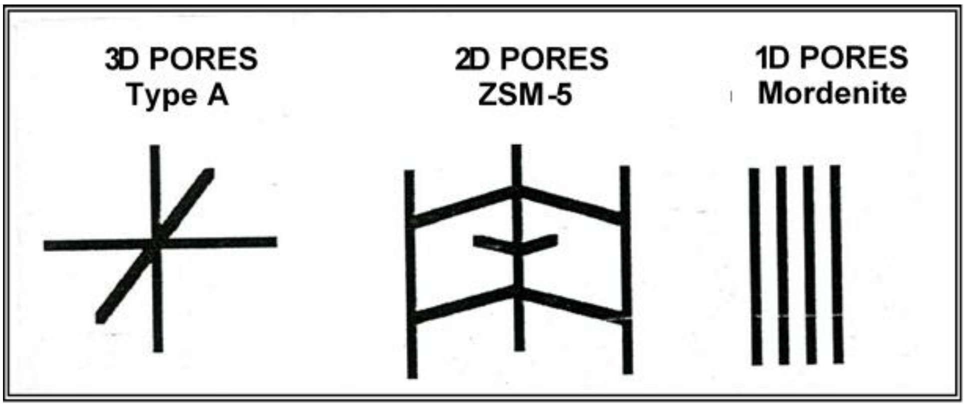

Fig. 7. Three commercial zeolites with different pore dimensionalities

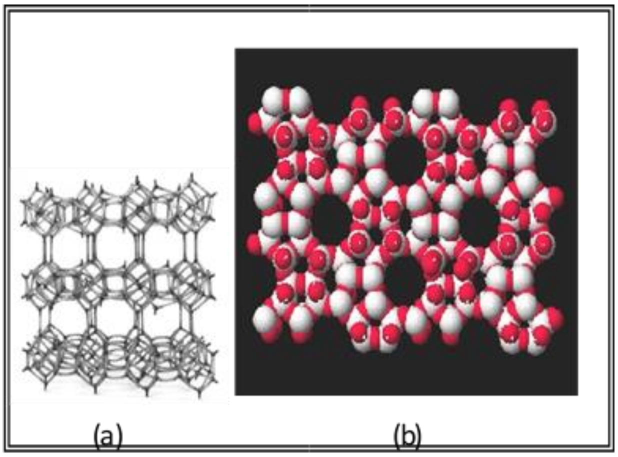

Fig. 8. a and b Skeletal Diagram for Zeolites

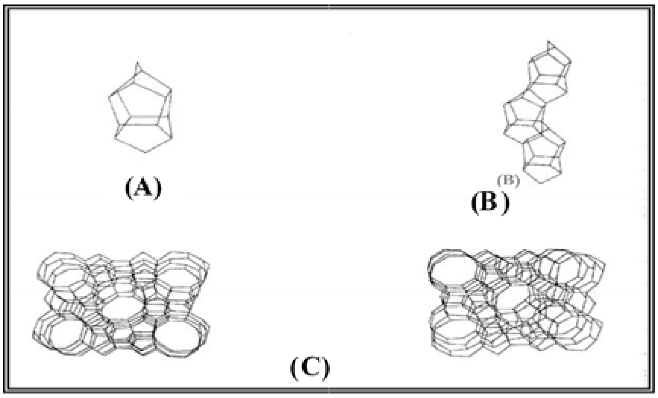

Fig. 9. Skeletal Diagram of (010) Face of ZSM-5

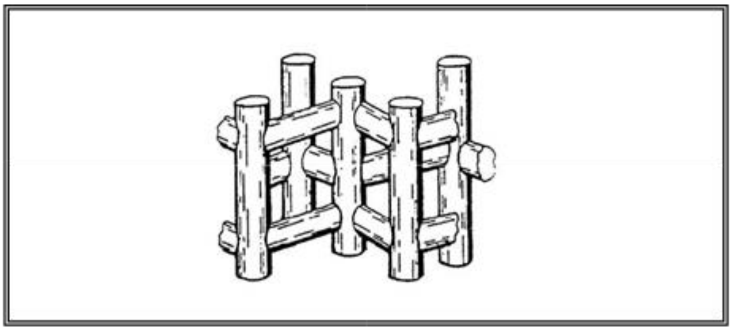

Fig. 10. Channel Structure of ZSM-5

ZSM-5 zeolite catalysts have facilitated the development of commercially significant petroleum and chemical processes. At room temperature, ZSM-5 can easily bind linear and monomethyl-substituted paraffin, but it can't handle bigger compounds like o-xylene and 2,2-dimethyl butane [96].

The composition-dependent properties of ZSM-5, such as ion exchange capacity, hydrophobicity, and catalytic activity, are influenced by its SiO_2/Al_2O_3 ratio. These properties exhibit a linear relationship with aluminum content. The SiO_2/Al_2O_3 ratio does not affect the X-ray pattern, pore size, volume, or framework structure.

As a catalyst, ZSM-5 exhibits a diverse array of unique properties, including the dewaxing of distillates, the synthesis of ethylbenzene, the isomerization of xylene, the disproportionation of toluene, and the conversion of methanol to MTBE [94]. Table 3 shows a set of previous studies on using zeolite in heavy metal removal.

Table 3. Summary of previous work, different types of catalysts used for heavy metal removal

Zeolite type	Heavy metal	Photocatalyst	Method/Process	Removal percentages	Reference
Zeolite Y	Cd, As, Cr, Cu, Pb, Ni, Mn, and Hg	Acids, bases, salts, surfactants, or metals		89.1% to 94.5%	[100]
ZnO-Zeolite Nanocomposite	Cd, Cu, Fe and Pb	ZnO	The degradation with Ultraviolet (UV) light exposure	98.96%, 95.43%, 96.07%, and 95.53%	[101]
Zeolite nanocomposite	Cr6+ and Cd2+	N-ZnO@Zeolite	Visible light	93% for Cr^{6+} and 89% for Cd^{2+}	[102]
Natural zeolites	Cr, Cu, Ni, Zn and Co			(434.78, 388 , 316 , 333.46 , 138.07 mg/g)	[103]
Natural zeolite	Rhodamine B	Zeo-TiO2 and Zeo-ZnO	UV-light	93.8%	[104]
Zeolite Beta (mBeta)	Cd2+ and Zn2+		Visible- light	-	[105]
Z-50	Tetracycline (TC)	CoS2/MoS2	Combination of ultrasonic and facile hydrothermal methods	-	[106]
Natural zeolite	MeO and potassium cyanide (CN) were removed	Zeolite/TiO_2	UV light radiation	(96.71%)	[84]
Zeolite Y	Fe, and As	TiO_2	UV light irradiation	90%, 30%, and 70%	[107]
ZIF-8 and ZIF-67	Pb^{2+} and Cu^{2+}			Pb^{2+} reach 1119.80 and 1348.42 mg/g, while they are 454.72 and 617.51 mg/g for Cu^{2+}	[108]
Cu-Zeolite	As			-	[109]
Zeolitic imidazolate framework-67 (ZIF-67)	Cr(VI)	TiO2 and ZnO	UV, visible (VIS), and NIR radiations	71.22%, 69.52%, and 40.79%	[110]
Natural Zeolitic	Cu (II)	Zeolite-Based TiO2 Composites	UV light	-	[111]

At each stage of catalyst development, the primary objective is to characterize the catalysts. Assess the efficacy of each operation by measuring critical parameters, which also function as specifications for future products. The researcher may examine or regulate the characterization of support properties, metal dispersion and location, and surface morphology [97].

A catalyst's quality depends on various factors, including stability, selectivity for specific products, and activity. These parameters are dependent on the catalyst preparation precursor conditions and reaction conditions. Understanding catalytic performance through the mechanism of catalytic action depends on looking at the chemical and physical properties of the substance itself and finding links between some of these properties and catalytic performance [98, 99].

The factors include acidity, specific surface area, pore structure, mechanical strength, and chemical stability. Other indispensable methods for characterizing supported metal catalysts are associated with metal dispersion and support location [94].

7- Conclusion

Operating costs, initial metal ion concentrations, environmental effects, pH levels, chemical usage, removal efficiency, and economic viability are some of the important factors that affect the choice of the best technique for eliminating heavy metal ions from wastewater. In order to comply with strict environmental regulations for the removal of heavy metals from industrial wastewater, this study has looked at several techniques, including coagulation/flocculation, ion exchange, flotation, membrane filtration, chemical precipitation, electrochemical treatment, adsorption, and photocatalysis. Of these techniques, photocatalysis has become an essential part of cutting-edge water treatment systems. Research on using photocatalytic technology to remove various heavy metal contaminants is currently thriving. Photocatalysts based on semiconductor oxides have attracted a lot of attention because of their remarkable photochemical stability, potent oxidizing capabilities, and nontoxicity, abundance, affordability, environmental friendliness, and chemical inertness.

The benefits of using aluminosilicate zeolite with a high Si/Al ratio in conjunction with other semiconductors to create photocatalytic composites are especially highlighted by this study. By adding zeolite to these semiconductor materials, their characteristics are improved, leading to better photocatalytic performance. High adsorption capacity, improved transparency, effective separation of photogenerated carriers, and ease of reclamation are among the advantages, all of which add to the overall increase in photocatalytic activity. Zeolite is a very promising alternative for developing immobilized photocatalytic materials that efficiently degrade heavy metals in wastewater, especially in light of the developments reported in this study. The results highlight how these novel composites can address environmental issues related to heavy metal contamination, opening the door for their widespread use in wastewater treatment system.

References

[1] S. Rahimi *et al.*, "Photocatalytic removal of cadmium (II) and lead (II) from simulated wastewater at continuous and batch system," *International Journal of Environmental Health Engineering,* vol. 3, no. 1, p. 31, 2014. https://doi.org/10.4103/2277-9183.139756

[2] A. J. M. Barros, S. Prasad, V. D. Leite, and A. G. Souza, "Biosorption of heavy metals in upflow sludge columns," *Bioresource Technology,* vol. 98, no. 7, pp. 1418-1425, 2007. https://doi.org/10.1016/j.biortech.2006.05.044

[3] V. Dhiman and N. Kondal, "ZnO Nanoadsorbents: A potent material for removal of heavy metal ions from wastewater," *Colloid and Interface Science Communications,* vol. 41, p. 100380, 2021. https://doi.org/10.1016/j.colcom.2021.100380

[4] N. A. Qasem, R. H. Mohammed, and D. U. Lawal, "Removal of heavy metal ions from wastewater: A comprehensive and critical review," *Npj Clean Water,* vol. 4, no. 1, pp. 1-15, 2021. https://doi.org/10.1038/s41545-021-00144-z

[5] J. Ayach *et al.*, "Comparing conventional and advanced approaches for heavy metal removal in wastewater treatment: an in-depth review emphasizing filter-based strategies," *Polymers,* vol. 16, no. 14, p. 1959, 2024. https://doi.org/10.3390/polym16141959

[6] M. M. Zareh, N. Metwally, and M. Abdel-Tawwab, "Review of Methods of Removal of Heavy Metals from Wastewater," *Bulletin of Faculty of Science, Zagazig University*, vol. 2024, no. 1, pp. 51-58, 2024. https://doi.org/10.21608/bfszu.2023.226989.1291

[7] X. Gao and X. Meng, "Photocatalysis for heavy metal treatment: A review," *Processes*, vol. 9, no. 10, p. 1729, 2021. https://doi.org/10.3390/pr9101729

[8] G. K. Kinuthia, V. Ngure, D. Beti, R. Lugalia, A. Wangila, and L. Kamau, "Levels of heavy metals in wastewater and soil samples from open drainage channels in Nairobi, Kenya: community health implications," *Scientific Reports*, vol. 10, no. 1, p. 8434, 2020. https://doi.org/10.1038/s41598-020-65359-5

[9] O. Faroon *et al.*, "Toxicological profile for cadmium," 2013.

[10] K. P. Gopinath, N. V. Madhav, A. Krishnan, R. Malolan, and G. Rangarajan, "Present applications of titanium dioxide for the photocatalytic removal of pollutants from water: A review," *Journal of Environmental Management*, vol. 270, p. 110906, 2020. https://doi.org/10.1016/j.jenvman.2020.110906

[11] B. Bakbolat *et al.*, "Recent developments of TiO2-based photocatalysis in the hydrogen evolution and photodegradation: a review," *Nanomaterials,* vol. 10, no. 9, p. 1790, 2020. https://doi.org/10.3390/nano10091790

[12] Z. Li, X. Meng, and Z. Zhang, "Recent development on MoS2-based photocatalysis: A review," *Journal of Photochemistry and Photobiology C: Photochemistry Reviews,* vol. 35, pp. 39-55, 2018. https://doi.org/j.jphotochemrev.2017.12.002

[13] D. Mukherjee, A. K. Ray, and S. Barghi, "Mechanism of acetyl salicylic acid (aspirin) degradation under solar light in presence of a TiO2-polymeric film photocatalyst," *Processes*, vol. 4, no. 2, p. 13, 2016. https://doi.org/10.3390/pr4020013

[14] H. Liang *et al.*, "3-D hierarchical Ag/ZnO@ CF for synergistically removing phenol and Cr (VI): heterogeneous vs. homogeneous photocatalysis," *Journal of colloid and interface science,* vol. 558, pp. 85-94, 2020. https://doi.org/10.1016/j.jcis.2019.09.105

[15] J. Safaei *et al.*, "Enhanced photoelectrochemical performance of Z-scheme g-C3N4/BiVO4 photocatalyst," *Applied Catalysis B: Environmental,* vol. 234, pp. 296-310, 2018. https://doi.org/10.1016/j.apcatb.2018.04.056

[16] X. Meng and Z. Zhang, "Bismuth-based photocatalytic semiconductors: Introduction, challenges and possible approaches," *Journal of Molecular Catalysis A: Chemical,* vol. 423, pp. 533-549, 2016. https://doi.org/10.1016/j.molcata.2016.07.030

[17] J.-Q. Wen, J.-M. Zhang, Z.-G. Qiu, X. Yang, and Z.-Q. Li, "The investigation of Ce doped ZnO crystal: the electronic, optical and magnetic properties," *Physica B: Condensed Matter,* vol. 534, pp. 44-50, 2018. https://doi.org/10.1016/j.physb.2018.01.035

[18] K. Harun, M. K. Yaakob, M. F. M. Taib, B. Sahraoui, Z. A. Ahmad, and A. A. Mohamad, "Efficient diagnostics of the electronic and optical properties of defective ZnO nanoparticles synthesized using the sol–gel method: experimental and theoretical studies," *Materials Research Express,* vol. 4, no. 8, p. 085908, 2017. https://doi.org/10.1088/2053-1591/aa8151

[19] Y. Zhao *et al.*, "Reduced graphene oxide supported ZnO/CdS heterojunction enhances photocatalytic removal efficiency of hexavalent chromium from aqueous solution," *Chemosphere,* vol. 286, p. 131738, 2022. https://doi.org/10.1016/j.chemosphere.2021.131738

[20] I. A. Salem, M. A. Salem, and M. A. El-Ghobashy, "The dual role of ZnO nanoparticles for efficient capture of heavy metals and Acid blue 92 from water," *Journal of Molecular Liquids,* vol. 248, pp. 527-538, 2017. https://doi.org/10.1016/j.molliq.2017.10.060

[21] B. Abebe, H. A. Murthy, and E. Amare, "Enhancing the photocatalytic efficiency of ZnO: Defects, heterojunction, and optimization," *Environmental nanotechnology, monitoring & management,* vol. 14, p. 100336, 2020. https://doi.org/10.1016/j.enmm.2020.100336

[22] İ. Demiral, C. Samdan, and H. Demiral, "Enrichment of the surface functional groups of activated carbon by modification method," *Surfaces and Interfaces,* vol. 22, p. 100873, 2021. https://doi.org/10.1016/j.surfin.2020.100873

[23] B. K. Reck, D. B. Müller, K. Rostkowski, and T. Graedel, "Anthropogenic nickel cycle: Insights into use, trade, and recycling," *Environmental science & technology,* vol. 42, no. 9, pp. 3394-3400, 2008. https://pubs.acs.org/doi/10.1021/es072108l

[24] C.-P. Wang, R. Franco, J. Moura, I. Moura, and E. Day, "The nickel site in active Desulfovibrio baculatus [NiFeSe] hydrogenase is diamagnetic. Multifield saturation magnetization measurement of the spin state of Ni (II)," *Journal of Biological Chemistry,* vol. 267, no. 11, pp. 7378-7380, 1992. https://doi.org/10.1016/S0021-9258(18)42527-6

[25] E. Denkhaus and K. Salnikow, "Nickel essentiality, toxicity, and carcinogenicity," *Critical reviews in oncology/hematology,* vol. 42, no. 1, pp. 35-56, 2002. https://doi.org/10.1016/S1040-8428(01)00214-1

[26] T. M. Nieminen, L. Ukonmaanaho, N. Rausch, and W. Shotyk, "Biogeochemistry of nickel and its release into the environment," *Nickel and its surprising impact in nature,* vol. 2, pp. 1-29, 2007. https://doi.org/10.1002/9780470028131.ch1

[27] L. Duro, M. Grivé, and E. Giffaut, "ThermoChimie, the ANDRA thermodynamic database," *MRS Online Proceedings Library (OPL),* vol. 1475, pp. 589-592, 2012. https://doi.org/10.1557/opl.2012.637

[28] P. B. Tchounwou, C. G. Yedjou, A. K. Patlolla, and D. J. Sutton, "Heavy metal toxicity and the environment," *Molecular, clinical and environmental toxicology: volume 3: environmental toxicology,* pp. 133-164, 2012. https://doi.org/10.1007/978-3-7643-8340-4_6

[29] S. Satarug and M. R. Moore, "Adverse health effects of chronic exposure to low-level cadmium in foodstuffs and cigarette smoke," *Environmental health perspectives,* vol. 112, no. 10, pp. 1099-1103, 2004.

[30] M. Rose, M. Baxter, N. Brereton, and C. Baskaran, "Dietary exposure to metals and other elements in the 2006 UK Total Diet Study and some trends over the last 30 years," *Food Additives and Contaminants,* vol. 27, no. 10, pp. 1380-1404, 2010. https://doi.org/10.1080/19440049.2010.496794

[31] B. Jezierska, K. Ługowska, and M. Witeska, "The effects of heavy metals on embryonic development of fish (a review)," *Fish physiology and biochemistry,* vol. 35, pp. 625-640, 2009. https://doi.org/10.1007/s10695-008-9284-4 ,

[32] M. C. SCIENTIST, "World's largest Science Technology & Medicine Open Access book publisher," 2017. http://dx.doi.org/10.5772/intechopen.69053

[33] A. K. Mishra and S. Ramaprabhu, "Study of CO_2 adsorption in low cost graphite nanoplatelets," 2010.

[34] M. he Zhang, Q. lin Zhao, X. Bai, and Z. fang Ye, "Adsorption of organic pollutants from coking wastewater by activated coke," *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* vol. 362, no. 1-3, pp. 140-146, 2010. https://doi.org/10.1016/j.colsurfa.2010.04.007

[35] H. Nourmoradi, M. Nikaeen, and M. Khiadani, "Removal of benzene, toluene, ethylbenzene and xylene (BTEX) from aqueous solutions by montmorillonite modified with nonionic surfactant: Equilibrium, kinetic and thermodynamic study," *Chemical engineering journal,* vol. 191, pp. 341-348, 2012. https://doi.org/10.1016/j.cej.2012.03.029

[36] E. Farsouni Eydi, A. Shariati, and M. R. Khosravi-Nikou, "Separation of BTEX compounds (benzene, toluene, ethylbenzene, and xylenes) from aqueous solutions using an adsorption process," *Journal of Dispersion Science and Technology,* vol. 40, no. 3, pp. 453-463, 2019. https://doi.org/10.1080/01932691.2018.1472007

[37] S. Nasrollahpour, D. Y. Kebria, M. Ghavami, and O. Ghasemi-Fare, "Application of organically modified clay in removing BTEX from produced water," in *Geo-Congress 2020*, 2020: American Society of Civil Engineers Reston, VA, pp. 275-283. https://doi.org/10.1061/9780784482827.031

[38] L. c. F. Lima, J. l. R. de Andrade, M. G. da Silva, and M. G. Vieira, "Fixed bed adsorption of benzene, toluene, and xylene (BTX) contaminants from monocomponent and multicomponent solutions using a commercial organoclay," *Industrial & Engineering Chemistry Research,* vol. 56, no. 21, pp. 6326-6336, 2017. https://doi.org/10.1021/acs.iecr.7b00173

[39] S. H. Lin and C. Y. Huang, "Adsorption of BTEX from aqueous solution by macroreticular resins," *Journal of hazardous materials,* vol. 70, no. 1-2, pp. 21-37, 1999. https://doi.org/10.1016/S0304-3894(99)00148-X

[40] J. M Ranck, R. S. Boman, J. L. Weeber L. E. katz, and E. J. Sullivaan S.-M. Zeolite, "BTEX Removal from Produced Water Using." *Journal of Environmental Engineering*. 2005. https://doi.org/10.1061/(ASCE)0733-9372(2005)131:3(434)

[41] M. Carvalho, M. Da Motta, M. Benachour, D. Sales, and C. Abreu, "Evaluation of BTEX and phenol removal from aqueous solution by multi-solute adsorption onto smectite organoclay," *Journal of hazardous materials*, vol. 239, pp. 95-101, 2012. https://doi.org/10.1016/j.jhazmat.2012.07.057

[42] F. Su, C. Lu, K. R. Johnston, and S. Hu, "Kinetics, thermodynamics, and regeneration of BTEX adsorption in aqueous solutions via NaOCl-oxidized carbon nanotubes," in *Environanotechnology*: Elsevier, 2010, pp. 71-97. https://doi.org/10.1016/B978-0-08-054820-3.00005-8

[43] F. Wang, M. Ruan, H. Lin, Y. Zhang, H. Hong, and X. Zhou, "Effects of ozone pretreatment on the formation of disinfection by-products and its associated bromine substitution factors upon chlorination/chloramination of Tai Lake water," *Science of the total environment*, vol. 475, pp. 23-28, 2014. https://doi.org/10.1016/j.scitotenv.2013.12.094

[44] X. Zhang, S. Echigo, H. Lei, M. E. Smith, R. A. Minear, and J. W. Talley, "Effects of temperature and chemical addition on the formation of bromoorganic DBPs during ozonation," *Water Research*, vol. 39, no. 2-3, pp. 423-435, 2005. https://doi.org/10.1016/j.watres.2004.10.007

[45] B. Kim, J. Anderson, S. Mueller, W. Gaines, and A. Kendall, "Literature review—efficacy of various disinfectants against Legionella in water systems," *Water research*, vol. 36, no. 18, pp. 4433-4444, 2002. https://doi.org/10.1016/S0043-1354(02)00188-4

[46] D. F. Ollis, "Photocatalytic purification and remediation of contaminated air and water," *Comptes Rendus de l'Académie des Sciences-Series IIC-Chemistry*, vol. 3, no. 6, pp. 405-411, 2000. https://doi.org/10.1016/S1387-1609(00)01169-5

[47] X. Chen, S. Shen, L. Guo, and S. S. Mao, "Semiconductor-based photocatalytic hydrogen generation," *Chemical reviews*, vol. 110, no. 11, pp. 6503-6570, 2010. https://doi.org/10.1021/cr1001645

[48] M. C. Manique, A. P. Silva, A. K. Alves, and C. P. Bergmann, "Application of hydrothermally produced TiO2 nanotubes in photocatalytic esterification of oleic acid," *Materials Science and Engineering: B*, vol. 206, pp. 17-21, 2016. https://doi.org/10.1016/j.mseb.2016.01.001

[49] G. Gokhroo *et al.*, "Observation of a near-threshold D 0 D¯ 0 π 0 enhancement in B→ D 0 D¯ 0 π 0 K decay," *Physical review letters*, vol. 97, no. 16, p. 162002, 2006. https://doi.org/10.1103/PhysRevLett.97.162002

[50] I. T. Peternel, N. Koprivanac, A. M. L. Božić, and H. M. Kušić, "Comparative study of UV/TiO2, UV/ZnO and photo-Fenton processes for the organic reactive dye degradation in aqueous solution," *Journal of hazardous materials*, vol. 148, no. 1-2, pp. 477-484, 2007. https://doi.org/10.1016/j.jhazmat.2007.02.072

[51] J.-M. Herrmann, "Fundamentals and misconceptions in photocatalysis," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 216, no. 2-3, pp. 85-93, 2010. https://doi.org/10.1016/j.jphotochem.2010.05.015

[52] X. Zhang, L. Song, X. Zeng, and M. Li, "Effects of electron donors on the TiO2 photocatalytic reduction of heavy metal ions under visible light," *Energy Procedia*, vol. 17, pp. 422-428, 2012. https://doi.org/10.1016/j.egypro.2012.02.115

[53] Y. Yang *et al.*, "Enhanced photocatalytic activity of hierarchical structure TiO_2 hollow spheres with reactive (001) facets for the removal of toxic heavy metal Cr (VI)," *RSC Advances*, vol. 4, no. 65, pp. 34577-34583, 2014. https://doi.org/10.1039/C4RA04787G

[54] L. Elleuch *et al.*, "A new insight into highly contaminated landfill leachate treatment using Kefir grains pre-treatment combined with Ag-doped TiO2 photocatalytic process," *Journal of hazardous materials*, vol. 382, p. 121119, 2020. https://doi.org/10.1016/j.jhazmat.2019.121119

[55] D. Cao *et al.*, "Enhanced the photoelectrocatalytic performance of TiO2 nanotube arrays by the synergistic sensitization of Ag–AgBr nanospheres," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 227, p. 117674, 2020. https://doi.org/10.1016/j.saa.2019.117674

[56] Y. Deng, Y. Xiao, Y. Zhou, T. Zeng, M. Xing, and J. Zhang, "A structural engineering-inspired CdS based composite for photocatalytic remediation of organic pollutant and hexavalent chromium," *Catalysis Today*, vol. 335, pp. 101-109, 2019. https://doi.org/10.1016/j.cattod.2018.09.012

[57] W. Jiang *et al.*, "An environment-friendly Strategy for one-step turning Cr (VI) Contaminant into a Cr-loaded Catalyst for CO2 utilization," *Advanced Sustainable Systems*, vol. 2, no. 4, p. 1700165, 2018. https://doi.org/10.1002/adsu.201700165

[58] F. Chen *et al.*, "Fabrication and characterization of ZnTiO3/Zn2Ti3O8/ZnO ternary photocatalyst for synergetic removal of aqueous organic pollutants and Cr (VI) ions," *Science of The Total Environment*, vol. 706, p. 136026, 2020. https://doi.org/10.1016/j.scitotenv.2019.136026

[59] X. Liu *et al.*, "Microwave-assisted synthesis of ZnO–graphene composite for photocatalytic reduction of Cr (VI)," *Catalysis Science & Technology*, vol. 1, no. 7, pp. 1189-1193, 2011. https://doi.org/10.1039/C1CY00109D

[60] T. Josué, L. Almeida, M. Lopes, O. Santos, and G. Lenzi, "Cr (VI) reduction by photocatalyic process: Nb2O5 an alternative catalyst," *Journal of Environmental Management*, vol. 268, p. 110711, 2020. https://doi.org/10.1016/j.jenvman.2020.110711

[61] A.-S. A. Al-Sherbini, H. E. Ghannam, G. M. El-Ghanam, A. A. El-Ella, and A. M. Youssef, "Utilization of chitosan/Ag bionanocomposites as eco-friendly photocatalytic reactor for Bactericidal effect and heavy metals removal," *Heliyon*, vol. 5, no. 6, 2019. https://doi.org/10.1016/j.heliyon.2019.e01980

[62] J. Ebrahimian, M. Mohsennia, and M. Khayatkashani, "Photocatalytic-degradation of organic dye and removal of heavy metal ions using synthesized SnO2 nanoparticles by Vitex agnus-castus fruit via a green route," *Materials Letters*, vol. 263, p. 127255, 2020. https://doi.org/10.1016/j.matlet.2019.127255

[63] D. Liu, M. Zhang, W. Xie, L. Sun, Y. Chen, and W. Lei, "Efficient photocatalytic reduction of aqueous Cr (vi) over porous BNNSs/TiO 2 nanocomposites under visible light irradiation," *Catalysis Science & Technology*, vol. 6, no. 23, pp. 8309-8313, 2016. https://doi.org/10.1039/C6CY01770C

[64] M. J.-C. Nalbandian, *Development and optimization of chemically-active electrospun nanofibers for treatment of impaired water sources*. University of California, Riverside, 2014. https://escholarship.org/uc/item/1vb2z5bn

[65] L. Pan *et al.*, "MOF-derived C-doped ZnO prepared via a two-step calcination for efficient photocatalysis," *Applied Catalysis B: Environmental*, vol. 189, pp. 181-191, 2016. https://doi.org/10.1016/j.apcatb.2016.02.066

[66] Y. Qu and X. Duan, "Progress, challenge and perspective of heterogeneous photocatalysts," *Chemical Society Reviews*, vol. 42, no. 7, pp. 2568-2580, 2013. https://doi.org/10.1039/C2CS35355E

[67] D. H. Arney, *Flux Synthesis of Photocatalytic Transition Metal Oxides*. North Carolina State University, 2011.

[68] K. Mori and H. Yamashita, "Progress in design and architecture of metal nanoparticles for catalytic applications," *Physical Chemistry Chemical Physics*, vol. 12, no. 43, pp. 14420-14432, 2010. https://doi.org/10.1039/C0CP00988A

[69] X.-G. Yan *et al.*, "Theoretical insight into the electronic and photocatalytic properties of Cu2O from a hybrid density functional theory," *Materials Science in Semiconductor Processing*, vol. 23, pp. 34-41, 2014. https://doi.org/10.1016/j.mssp.2014.02.023

[70] B. L. Ellis, P. Knauth, and T. Djenizian, "Three-dimensional self-supported metal oxides for advanced energy storage," *Advanced Materials*, vol. 26, no. 21, pp. 3368-3397, 2014. https://doi.org/10.1002/adma.201306126

[71] K. Sardar and R. I. Walton, "Hydrothermal synthesis map of bismuth titanates," *Journal of solid state chemistry*, vol. 189, pp. 32-37, 2012. https://doi.org/10.1016/j.jssc.2012.01.017

[72] M. B. Tahir, H. Kiran, and T. Iqbal, "The detoxification of heavy metals from aqueous environment using nano-photocatalysis approach: a review," *Environmental Science and Pollution Research*, vol. 26, no. 11, pp. 10515-10528, 2019. https://doi.org/10.1007/s11356-024-34257-y

[73] X. Chen and S. S. Mao, "Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications," *Chemical reviews*, vol. 107, no. 7, pp. 2891-2959, 2007. https://doi.org/10.1021/cr0500535

[74] D. Chen, M. Sivakumar, and A. K. Ray, "Heterogeneous photocatalysis in environmental remediation," *Developments in Chemical Engineering and Mineral Processing*, vol. 8, no. 5-6, pp. 505-550, 2000. https://doi.org/10.1002/apj.5500080507

[75] D. Chen and A. K. Ray, "Removal of toxic metal ions from wastewater by semiconductor photocatalysis," *Chemical Engineering Science*, vol. 56, no. 4, pp. 1561-1570, 2001. https://doi.org/10.1016/S0009-2509(00)00383-3

[76] Z. Shen *et al.*, "Direct conversion of formaldehyde to ethylene glycol via photocatalytic carbon–carbon coupling over bismuth vanadate," *Catalysis Science & Technology*, vol. 6, no. 17, pp. 6485-6489, 2016. https://doi.org/10.1039/C6CY01468B

[77] D. Bokov *et al.*, "Nanomaterial by sol-gel method: synthesis and application," *Advances in materials science and engineering*, vol. 2021, no. 1, p. 5102014, 2021. https://doi.org/10.1155/2021/5102014

[78] W. Nachit *et al.*, "Synthesis of nanosized TiO2 powder by sol gel method at low temperature," *Molecular Crystals and Liquid Crystals*, vol. 627, no. 1, pp. 170-175, 2016. https://doi.org/10.1080/15421406.2015.1137135

[79] M. Parashar, V. K. Shukla, and R. Singh, "Metal oxides nanoparticles via sol–gel method: a review on synthesis, characterization and applications," *Journal of Materials Science: Materials in Electronics*, vol. 31, no. 5, pp. 3729-3749, 2020. https://doi.org/10.1007/s10854-020-02994-8

[80] M. H. Sosa Lissarrague, S. Alshehri, A. Alsalhi, V. L. Lassalle, and I. López Corral, "Heavy metal removal from aqueous effluents by TiO2 and ZnO nanomaterials," *Adsorption Science & Technology*, vol. 2023, p. 2728305, 2023. https://doi.org/10.1155/2023/2728305

[81] M. Shirzad Siboni, M.-T. Samadi, J.-K. Yang, and S.-M. Lee, "Photocatalytic removal of Cr (VI) and Ni (II) by UV/TiO2: kinetic study," *Desalination and water treatment*, vol. 40, no. 1-3, pp. 77-83, 2012. https://doi.org/10.1080/19443994.2012.671144

[82] S. Liu, J.-H. Yang, and J.-H. Choy, "Microporous SiO2–TiO2 nanosols pillared montmorillonite for photocatalytic decomposition of methyl orange," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 179, no. 1-2, pp. 75-80, 2006. https://doi.org/10.1016/j.jphotochem.2005.07.016

[83] O. M. Kalfa, Ö. Yalçınkaya, and A. R. Türker, "Synthesis of nano B2O3/TiO2 composite material as a new solid phase extractor and its application to preconcentration and separation of cadmium," *Journal of Hazardous Materials*, vol. 166, no. 1, pp. 455-461, 2009. https://doi.org/10.1016/j.jhazmat.2008.11.112

[84] H. Koohestani, M. Hassanabadi, H. Mansouri, and A. Pirmoradian, "Investigation of photocatalytic performance of natural zeolite/TiO2 composites," *Micro & Nano Letters*, vol. 14, no. 6, pp. 669-673, 2019. https://doi.org/10.1049/mnl.2018.5754

[85] R. Gayatri, T. E. Agustina, D. Bahrin, R. Moeksin, and G. Gustini, "Preparation and characterization of ZnO-zeolite nanocomposite for photocatalytic degradation by ultraviolet light," *Journal of Ecological Engineering*, vol. 22, no. 2, pp. 178-186, 2021. https://doi.org/10.12911/22998993/131031

[86] P. Zawadzki, E. Kudlek, and M. Dudziak, "Kinetics of the photocatalytic decomposition of bisphenol a on modified photocatalysts," *Journal of Ecological Engineering*, vol. 19, no. 4, 2018. https://doi.org/10.12911/22998993/89651

[87] T. E. Agustina, E. Melwita, D. Bahrin, R. Gayatri, and I. F. Purwaningtyas, "Synthesis of nano-photocatalyst ZnO-natural zeolite to degrade procion red," *International Journal of Technology*, vol. 11, no. 3, 2020. https://doi.org/10.14716/ijtech.v11i3.3800

[88] I. Bankos, J. Valyon, G. Kapustin, D. Kallo, A. Klyachko, and T. Brueva, "Acidic and catalytic properties of hydrogen sodium mordenite," *Zeolites*, vol. 8, no. 3, pp. 189-195, 1988. https://doi.org/10.1016/S0144-2449(88)80306-3

[89] J. D. Sherman, "Synthetic zeolites and other microporous oxide molecular sieves," *Proceedings of the National Academy of Sciences*, vol. 96, no. 7, pp. 3471-3478, 1999. https://doi.org/10.1073/pnas.96.7.3471

[90] M. Musa, V. Tarina, A. Stoica, E. Ivanov, D. Plostinaru, and E. Pop, "Gr. Pop, R. Ganea, R. Birjega, G. Musca and E. Paukshtis," *Zeolites*, vol. 7, p. 427, 1987. https://doi.org/10.1016/0144-2449(87)90009-1

[91] S. Bhatia, J. Beltramini, and D. Do, "Deactivation of zeolite catalysts," *Catalysis Reviews—Science and Engineering*, vol. 31, no. 4, pp. 431-480, 1989. https://doi.org/10.1080/01614948909349937

[92] P. Weisz and V. Frilette, "Intracrystalline and molecular-shape-selective catalysis by zeolite salts," *The Journal of Physical Chemistry*, vol. 64, no. 3, pp. 382-382, 1960. https://doi.org/10.1021/j100832a513

[93] P. Weisz, "Molecular Shape Selective Catalysis," *Proceedings 7th Intern. Congr. on Catal*, no. Part A, p. 3, 1980. https://doi.org/10.1016/S0167-2991(09)60257-3

[94] John H. Sinfelt, "Structure of Metallic Catalysis," ed American Physical Society (APS), 1979. https://doi.org/10.1103/RevModPhys.51.569

[95] D. Olson, G. Kokotailo, S. Lawton, and W. Meier, "Crystal structure and structure-related properties of ZSM-5," *The Journal of Physical Chemistry*, vol. 85, no. 15, pp. 2238-2243, 1981. https://doi.org/10.1021/j150615a020

[96] J. Gray and J. Cobb Jr, "Hydroisomerization and hydrocracking of normal pentane over various mordenite catalysts," *Journal of Catalysis*, vol. 36, no. 2, pp. 125-141, 1975. https://doi.org/10.1016/0021-9517(75)90018-4

[97] J. R. Anderson and M. Boudart, *Catalysis: science and technology*. Springer Science & Business Media, 2012.

[98] A. Zonenberg, W. Zarzycki, and M. Leoniak, "The effect of Chernobyl accident on the development of malignant diseases-situation after 20 years," *Endokrynologia Polska*, vol. 57, no. 3, pp. 244-252, 2006.

[99] R. Szostak, "Secondary synthesis methods," in *Studies in Surface Science and Catalysis*, vol. 137: Elsevier, 2001, pp. 261-297. https://doi.org/10.1016/S0167-2991(01)80248-2

[100] M. S. Hakim *et al.*, "A Review on Development of Porous Aluminosilicate-Based Zeolite Adsorbent for Heavy Metal Pollution Treatment," *Jurnal Sains Materi Indonesia*, vol. 25, no. 2, pp. 85-99, 2024. https://doi.org/10.55981/jsmi.2024.1076

[101] T. K. Ramadhini, T. E. Agustina, E. Melwita, and M. S. Wijayanti, "Photocatalytic degradation of heavy metals Cd, Cu, Fe and Pb using ZnO-zeolite nanocomposite," *Indonesian Journal of Environmental Management and Sustainability*, vol. 7, no. 4, pp. 147-152, 2023. https://doi.org/10.26554/ijems.2023.7.4.147-152

[102] M. Rani, U. Shanker, and M. Sillanpää, "Green synthesis of N-doped ZnO@ Zeolite nanocomposite for the efficient photo-adsorptive removal of toxic heavy metal ions Cr6+ and Cd2+," *Inorganic Chemistry Communications*, vol. 157, p. 111401, 2023. https://doi.org/10.1016/j.inoche.2023.111401

[103] M. Irannajad and H. Kamran Haghighi, "Removal of heavy metals from polluted solutions by zeolitic adsorbents: a review," *Environmental Processes*, vol. 8, pp. 7-35, 2021. https://doi.org/10.1007/s40710-020-00476-x

[104] F. Alakhras, E. Alhajri, R. Haounati, H. Ouachtak, A. A. Addi, and T. A. Saleh, "A comparative study of photocatalytic degradation of Rhodamine B using natural-based zeolite composites," *Surfaces and Interfaces*, vol. 20, p. 100611, 2020. https://doi.org/10.1016/j.surfin.2020.100611

[105] M. Wang, H. Yao, L. Zhang, and X. Zhou, "Synthesis of highly-efficient photocatalyst for visible-light-driven hydrogen evolution by recycling of heavy metal ions in wastewater," *Journal of hazardous materials*, vol. 383, p. 121149, 2020. https://doi.org/10.1016/j.jhazmat.2019.121149

[106] J. Liu, H. Lin, Y. He, Y. Dong, and E. R. G. Y. Menzembere, "Novel CoS2/MoS2@ Zeolite with excellent adsorption and photocatalytic performance for tetracycline removal in simulated wastewater," *Journal of Cleaner Production*, vol. 260, p. 121047, 2020. https://doi.org/10.1016/j.jclepro.2020.121047

[107] M. K. Kim, S.-H. Pak, M. C. Shin, C.-g. Park, E. Magnone, and J. H. Park, "Development of an advanced hybrid process coupling TiO 2 photocatalysis and zeolite-based adsorption for water and wastewater treatment," *Korean Journal of Chemical Engineering*, vol. 36, pp. 1201-1207, 2019. https://doi.org/10.1007/s11814-019-0300-4

[108] Y. Huang, X. Zeng, L. Guo, J. Lan, L. Zhang, and D. Cao, "Heavy metal ion removal of wastewater by zeolite-imidazolate frameworks," *Separation and Purification Technology*, vol. 194, pp. 462-469, 2018. https://doi.org/10.1016/j.seppur.2017.11.068

[109] M. Khatamian, N. Khodakarampoor, and M. Saket-Oskoui, "Efficient removal of arsenic using graphene-zeolite based composites," *Journal of colloid and interface science*, vol. 498, pp. 433-441, 2017. https://doi.org/10.1016/j.jcis.2017.03.052

[110] H. Park *et al.*, "Zeolitic imidazolate framework-67 (ZIF-67) rhombic dodecahedrons as full-spectrum light harvesting photocatalyst for environmental remediation," *Solid State Sciences*, vol. 62, pp. 82-89, 2016. https://doi.org/10.1016/j.solidstatesciences.2016.10.018

[111] A. Peter *et al.*, "Photocatalytic efficiency of zeolite-based TiO2 composites for reduction of Cu (II): kinetic models," *International Journal of Applied Ceramic Technology*, vol. 11, no. 3, pp. 568-581, 2014. https://doi.org/10.1111/ijac.12046

إزالة المعادن الثقيلة من مياه الصرف عبر تفاعل التحفيز الضوئي: ورقة مراجعة

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الخلاصة

يعتمد بيئة نظيفة وصحة الإنسان على إزالة أيونات المعادن الثقيلة من مياه الصرف الصحي. الأنظمة البيئية والصحة العامة مهددة بشدة بأيونات المعادن الثقيلة، مثل النيكل(Ni) ، الرصاص(Pb) ، الكادميوم (Cd)، الفاناديوم(V) ، الكروم(Cr) ، والنحاس (Cu). على سبيل المثال، بسبب تأثيراته السامة، يُسمح بالكادميوم فقط بتركيز ٠,٠٠٥ ملغ/لتر في مياه الشرب، بينما يُسمح بالرصاص بتركيز أقصى قدره ٠,٠١٥ ملغ/لتر. تم استخراج أيونات المعادن الثقيلة من أنواع مختلفة من مياه الصرف الصحي باستخدام مجموعة متنوعة من الطرق، مثل الامتزاز، والترشيح الغشائي، والإضافة الكيميائية، والمعالجة الكهروكيميائية، والتحفيز الضوئي.

ومع ذلك، غالبًا ما تواجه التقنيات التقليدية عقبات مثل التكاليف التشغيلية الباهظة والفعالية المحدودة، حيث تنخفض معدلات الإزالة أحيانًا إلى أقل من ٧٠%. يمكن أن تؤدي هذه التقنيات أيضًا إلى إنتاج نواتج ثانوية خطرة، مما يجعل إجراءات معالجة مياه الصرف الصحي أكثر صعوبة. نظرًا لأن التحفيز الضوئي متعدد الاستخدامات في معالجة البيئة، يمكن استخدامه لإزالة المعادن الثقيلة. قدرة الهياكل النانوية شبه الموصلة القائمة على أكاسيد المعادن على إزالة المعادن الثقيلة بفعالية من المياه الملوثة قد حظيت باهتمام مؤخرًا. على سبيل المثال، عند تعرضها لأطوال موجية معينة من الضوء، يمكن لأكسيد الزنك (ZnO) وثاني أكسيد التيتانيوم (TiO2)إزالة بعض المعادن الثقيلة بكفاءات تصل إلى ٩٥%. تم استخدام الزيوليت بشكل متزايد في معالجة مياه الصرف الصحي على مدى العشرين عامًا الماضية؛ وقد أظهرت التطبيقات قدرات إزالة تصل إلى ١٠٠ ملغ/غ للكبريت و ١٥٠ ملغ/غ للرصاص. تتناول هذه المقالة التطورات الأخيرة في استخدام الزيوليتات لاستخراج المعادن الثقيلة من المحاليل الملوثة. تم تجميع ومناقشة كل من طرق معالجة مياه الصرف التقليدية والحديثة في هذا التحليل الشامل، بما في ذلك تطبيق زيوت ZSM-5 في تقنية التحفيز الضوئي، والتي يمكن أن تقلل من تكاليف التشغيل بنسبة تصل إلى ٣٠% وتحسن كفاءات الإزالة. بغض النظر عن كل شيء، فإن دمج الزيوليت مع الأنظمة الضوئية التحفيزية هو استراتيجية قابلة للتطبيق لزيادة فعالية معالجة المعادن الثقيلة في معالجة مياه الصرف الصحي.

الكلمات الدالة: الكادميوم، أيونات المعادن الثقيلة، النيكل، المحفز الضوئي، مياه الصرف الصحي.