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An overview of analytical techniques for heavy metal ion detection and removal from industrial sewage

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Abstract— Removal of heavy metal ions from wastewater is of paramount importance for a clean environment and human health. Various reported processes have addressed the removal of heavy metal ions from various wastewater sources. These processes can be divided into adsorption, membrane, chemical, electrical, and photo catalytic processes. This article provides a comprehensive and critical overview of these methods, discussing the media/sorbents used, removal efficiency, operating conditions, and advantages and disadvantages of each method. We also summarize the main results of previous studies reported in the literature. It should be noted that recent research has generally focused on adsorption techniques. The main obstacles to the adsorption process are the ability to simultaneously remove different types of ions, the long retention time of the adsorbent and cycle stability. Although chemical and membrane processes are practical, high levels of sludge formation and post-treatment requirements are key issues that must be addressed in chemical processes. Suppression of fouling and scaling can further improve membrane separation. However, pretreatment and regular cleaning of the membrane incurs additional costs. Electrical methods have also been reported to be efficient. However, in addition to overcoming the problem of massive sludge formation, industrial scale separation is required. Electrical and photo catalytic-based methods are not yet mature. Future research should focus on environmentally friendly, inexpensive, and sustainable materials and methods.

Keywords: industrial sewage, heavy metals, spectrophotometric analysis, removal methods, removal efficiency.

I. INTRODUCTION

Rapid development in science and technology has made the automotive industry a rapidly advancing industry [43]. In recent years, a fast advancement in automotive industries has resulted in increased production, which made high quantity emission of wastewater to the geo environment [39]. Automotive industries are one of the main resources causing major issuers to mature by emitting hazardous wastewater [10]. Automotive industries are the main consumer of water for several purposes and productive levels where vehicles are cleaned, treated, washed, and colored, producing a mass volume of wastewater [13]. The most generally discovered pollutants in effluents are organic and inorganic contaminants, total suspended solids like detergents, paint, metal, grease, acid and biological oxygen demand and chemical oxygen demand [4]. Heavy metal emissions from wastewater are evolving with a rise of industry and human endeavors [14] such as plating and electroplating, batteries, pesticides, mining, sugarcane industry, metal rinsing process, tanning industry, fluidization bed bioreactors, textile industry, metal smelting, petrochemicals, papermaking, and electrolysis applications [36]. Heavy metal-contaminated effluent enters the soil and waterways, endangering human health and ecosystems [28]. Heavy metal is not biodegradable and may be carcinogenic [30]. Therefore, these metals are present in inappropriate amounts in water [19]. It can cause serious health problems for organisms. Lead (Pb), Zinc (Zn), and mercury are the most common heavy metals [34]. Major sources of heavy metals, health effects, and drinking water allowance [29]. Heavy metals along with their permitted level and effect of the material is elaborated Table 1.

Table 1: Heavy metals - Sources and permitted level.

Heavy Metals	Permitted Range (µg)	Source	Acute Exposure	Chronic Exposure
Arsenic (As)	10	Production of electronics and glass	Diarrhoea, neuropathy, vomiting, encephalopathy.	liver cancer, lungs cancer, skin cancer
Cadmium (Cd)	3	Industries of paint, steel, plastic and metal.	pneumonitis	Lungs cancer, fibrosis.
Chromium (Cr)	50	Tanneries, pulp and steel mills	Acute renal failure, haemolysis.	Lungs cancer, pulmonary fibrosis.
Cobalt (Co)	2.3	By products of Copper or nickel	Cardiomyopathy	Pneumoconiosis
Copper (Cu)	2000	Industry of electronic and cables, Corroded plumbing systems.	Haemolysis, Blue vomitus, haemorrhage.	Wilson disease, Vineyard sprayer's lung.
Iron (Fe)	2	Steel industry	Metabolic acidosis, vomiting, cardiac depression.	Hepatic cirrhosis
Lead (Pb)	10	Alloys, glazes, pigments, plastic stabilizers.	kidney and brain damage	Cardiovascular system, kidney, lungs, bones
Manganese (Mn)	1.8	Mine quarry operation, and industrial effluent discharge.	MFF (inhaled)	neuropsychiatric
Mercury (Hg)	6	Production of electrolytic of caustic soda and chlorine, electrical applications.	Vomiting, fever, diarrhoea.	Neuropsychiatric, Parkinson-like syndrome respiratory
Nickel (Ni)	70	Production of nickel alloy and stainless steel.	Myocarditis, encephalopathy.	Reduced sperm count, pulmonary fibrosis.
Zinc (Zn)	3000	Cosmetics, brass coating, and rubber products.	Vomiting, diarrhoea, and MFF	Anaemia, neurologic degeneration.

Sourse: own elaboration.

Industrial sewage is a pressing problem that has plagued communities around the world [23]. With increased industrial activity, wastewater often contains pollutants such as metals, oils, and toxins that can create serious environmental and public health issues [11]. Industrial wastewater treatment is a complex set of processes used to separate and remove pollutants [12]. While the traditional methods of industrial wastewater treatment may not be able to remove all the contaminants, metal ion analysis provides a more comprehensive approach. This research paper explores the potential of metal ion analysis to revolutionize industrial sewage treatment and how it can help improve public safety and environmental health.

This survey paper is arranged as follow; in section 2 heavy metal wastewater treatment techniques are described. In section 3 remarks of heavy metal treatment methods are described. In section 4 concluded with conclusion.

II. HEAVY METAL WASTEWATER TREATMENT METHODS

In this in-progress section, several heavy metal removal methods have been clearly described.

a. Precipitation with chemicals

Because it is effective, simple to operate, and economical, precipitation with chemicals is the most extensively utilized technique in the business. Chemicals react with heavy metal ions to generate an insoluble precipitate during the precipitation process. Sedimentation or filtering can be used to separate the precipitate from the water. The treated water is then decanted and released or reused properly. Hydroxide precipitation and sulfide precipitation are two common chemical precipitation processes. Schematic diagram of Chemical precipitation is shown in Figure 1.

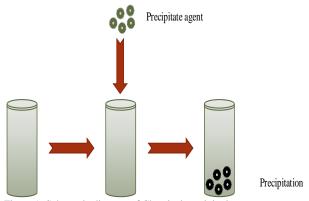


Figure 1: Schematic diagram of Chemical precipitation. Sourse: own elaboration.

1. Precipitation with Hydroxide

Metal hydroxides are formed during the precipitation with hydroxide as a result of hydroxide reactions involving heavy metals. Industrial and remediation processes produce waste water containing chelated heavy metals. Both hazardous heavy metals and the chelating agents must be removed from wastewater containing chelated heavy metals. In recent years, the treatment of wastewater containing extremely stable chelated heavy metals has become a contentious and challenging issue.

Fu, Fenglian, et al. [15] suggested a novel method to deal with wastewater containing chelated heavy metals called the Advanced Fenton Chemical Precipitation Process (AF-CPP) to address this issue. In this method, chelate complexes are broken down using zero valent Iron and hydrogen peroxide, and then heavy metals are precipitated in an alkaline solution.

Lime is used as a precipitant by Chen et al. [9] to extract Copper, Zinc, Chromium, and lead from sewage. Cheap lime is used as a seed material and also added fly ash. Due to the relatively high dosages of lime, the use of CaO as a precipitant has several restrictions. Between pH 7 and 11, the authors claim clearance efficiencies of 99.37% to 99.69%. Using ferrous Sulphate and sulphuric acid to acquire and remove Cr(VI) ions, Mirbagheri and Hosseini [27] precipitated Cr(VI) to Cr (III) using Ca(OH)2 and NaOH. The maximum conversion was accomplished with Ca(OH)2 at pH 2.0-2.3, and the largest precipitation of Cr(III) at pH 8.7. Removal efficiency ranged from 98.56% to 99.9% when chromium concentrations were lowered from 30 mg/l to 0.01 mg/l and copper concentrations were reduced from 48.51 mg/l to 0.694 mg/l. Heavy metal removal through chemical precipitation is detailed inTable 2.

Table 2: Heavy metal removal through chemical precipitation.

Author	Heavy metal	Precipitant	Optimum pH	Initial metal concentration	Removal efficiency (%)
Fu, Fenglian, et al.[18]	Cu	1,3,5 Hexa hydro triazine di thio-carbonate	3 to 9	100 mg/L	99.6
Fu, Fenglian, et al.[19]	Ni	Alkali	2.5	50 mg/L	98.4
Fu, Fenglian, et al. [20]	Ni	Alkali	11	50 mg/L	92.8
Chen, Quanyuan, et al. [21]	Cu, Zn, Cr, Pb	Lime	7 to 11	100 mg/L	99.3 to 99.6
Mirbagheri, S. Ahmad, and SeyedNezamedinHosseini. [22]	Cu, Cr	Calcium Hydroxide and Sodium Hydroxide	8.7 and 12	48.51 mg/L	98.56
Matlock, Matthew M., et al. [23]	Cu, Cd	Pyridine Based Thiol Ligand	4.5	200 mg/L	99.99, 99.88
Matlock, Matthew M., et al.[24]	Fe	1,3 – Benzene Diamido Ethane Thioldi Anion	4.5	194 mg/L	90
Shih, Yu-Jen, et al. [25]	Ni	Ferric Sulphate	3	100 mM	99.9
Jiang, Chun-yu, et al.[26]	Cu	Calcium Hydroxide	12 to 13	25 mg/L	99
Mauchauffée, et al. [27]	Cu, Cd, Ni, Zn, Pb	Sodium Deaconate	4 to 8	-	90
Azabou, Samia, et al. [28]	Zn	Sulfate Reducing Bacteria	6.8	200 mg/L	-
Alvarez, Maria Teresa, et al. [29]	Cu, Zn, Pb	Hydrogen Sulphide	3		94
Guo, Zhen-Ren, et al. [30]	Cr	Calcium Oxide (Cao) and Magnesium Oxide (Mgo)	8		99
Blue, Lisa Y., et al. [31]	Hg	1,3 – Benzene Diamido Ethane Thiolate	4.7 and 6.4		99.9

Sourse: own elaboration.

Due to the production of secondary wastes such metal hydroxide sludge and gypsum, hydroxyl precipitation has some drawbacks, including the necessity for expensive disposal. Amphoteric metal hydroxides are some of them.

2. Precipitation with Sulfide

It is also an excellent treatment technique for hazardous heavy metal complexes. One of the key advantages of employing Sulphides is that metal Sulphide precipitates are significantly less soluble than hydroxide precipitates, and Sulphide precipitates are not amphoteric. As a result, the Sulphide precipitation technique is capable of removing a substantial amount of metal. When compared to hydroxide precipitation, the pH range is wider. Metal Sulphide sludge has greater thickening and dewatering capabilities than metal hydroxide slurries. In sulfide precipitation, sulfide compounds react with heavy metals to form an insoluble precipitate. Sulfide precipitation has several advantages, including selective removal of heavy metals, faster reaction rate, improved sedimentation properties, sulfide sediment can be reused by smelting.

To remove copper and cadmium, Matlock., et al. [25] used pyridine-based thiol ligands, which have several advantages, including the availability of many heavy metal removal sites and the formation of stable metal ligand precipitates. It is a sulphur-containing ligand that binds to heavy metals to form stable precipitates. Heavy metals and any terminal sulphur groups can interact with this ligand because of its sufficient length. Thus, his 99.99% removal of Copper and his 99.88% removal of Cadmium were obtained at optimal pH 4.5 and 6, respectively.

Matlock, Matthew M., et al. [24] designed a1,3-benzene diamide ethane thioldi anion (BDET) to selectively and irreversibly binds of heavy metals from aqueous solutions. According to a recent study, AMD samples were collected at an abandoned mine in Pikeville, Kentucky, had more over 90% of several harmful or problematic elements eliminated by BDET. At pH 4.5, the concentration of metals, such as Iron, can be lowered from 194 parts per million to less than 0.009 parts per million.

The effluents from electroless nickel plating frequently contain citric acid chelate complexes and co-existing hypo phosphites, which are hydroxyl radical scavengers and frequently catalyse the Fenton reaction between H2O2 and Fe2+. As a result, according to Shih, Yu-Jen, et al. [38], the citrate was cleaned up using the Fered-Fenton process and freed nickel ions were eliminated using the alkaline precipitation method. The COD for citric acid is a current density of 190 Am–2.99.9 % of the nickel released from citrate chelate ion has been removed by cathodic deposition followed by precipitation. Hypo phosphate did not significantly affect COD or nickel removal efficiency. The COD removal rate of wastewater from the electro less nickel plating process is as high as 93%, confirming the feasibility of the Fered-Fenton process.

Jiang, Chun-yu, and colleagues [20] investigated heavy metal-resistant isolates from heavy metal-contaminated soil that were identified as Burkholderia species using J62 based on 16Sr DNA gene sequence analysis. The isolates were tested for heavy metal and antibiotic resistance, as well as heavy metal solubilization. The isolates also went through pot tests to see whether they could improve plant growth as well as Pb and Cd absorption from heavy metal-contaminated soils. When compared to uninoculated controls, inoculated plants showed increases in tissue lead and cadmium levels ranging from 38% to 192% and 5% to 191%, respectively.

Traditional methods of removing heavy metals from industrial wastewaters include chemical precipitation. This process results in sludge with no commercial value that is dumped into special landfills. Using Sodium decanoate, Mauchauffée et al. [26] discuss investigations on the possibility of executing elective precipitation of binary mixes of metal cations. To begin, the solubility products of the six metal decanoates are calculated. Before testing their solubility in pure water at 20°C, these six compounds were produced and controlled. Ksp values for Cd, Cu, Mn, Ni, Pb, and Zn decanoate s are 10-11.69, 10-14.65, 10-10.16, 10-9.17, 10-16.05, and 10-13.05, respectively.

Azabou, Samia, et al.'s study [3] examined sulfate-reducing bacteria (SRB) mixed culture for heavy metal resistance and precipitation. In a prior work, gypsum phosphate was used as a Sulphate source to enhance these bacteria from sewage sludge. Sulphate and Zinc are both naturally present in gypsum phosphate, so to test the Zinc tolerance of SRB, a synthetic formulation comprising 20 mm Sulphate and 200 mg/L of Zinc chloride was tested in medium. Zinc resistance was determined by monitoring susceptibility to bacterial growth and Zinc removal. Bacterial growth and sulfate reduction were possible at initial Zinc concentrations between 10 and 150 mg/L. Zinc concentrations above 150 mg/L were lethal for SRB.

The biological production of hydrogen sulfide (H2S) by SRB has important potential with in environmental biotechnology. As a result, Alvarez, Maria Teresa, et al. [2] explore the viability of utilising SRB for the treatment of AMD on a small scale. This process was divided into three stages: enhancing HS production through the use of total volatile fatty acids (TVFA) by SRB, establishing a biofilm reactor for sulfide production, and precipitating metals using biologically produced HS. Papaya, apple, and banana were used as the substrate for TVFA production. H2S generated during TVFA decomposition was used to precipitate metal-contaminated wastewater collected from the Bolivarmine (Oruro, Bolivia). The highest H2S concentration measured was around 16 mm. Copper separation efficacy was approximately 100%, zinc separation efficiency was over 94%, and lead separation efficiency was over 92%.

3. Chelating precipitation

The typical chemical precipitation process is another name for it. Due to conventional use, there are various limitations and it is getting harder and harder to comply with severe environmental standards. heavy metal wastewater sedimentation treatment, particularly by coordinated agents. Chelating precipitates are widely used in many sectors to remove heavy metals from aqueous environments.

Fu, Fenglian, et al. [17] prepared a new di thio carbamate-based heavy metal element called 1,3,5-hexahydrotriazinedithiocarbamate (HTDC). It is utilized to eliminate coordinated Copper from the wastewater. The prepared HTDC has high effective function. The prepared element effectively remove the Copper to lower than 0.5 mg/L from the synthetic and industrial waste water consisting the Copper in the pH level of 3 to 9.

It is difficult to remove Ni(II) from the Nickel Ethylene Diamine Tetra Acetic Acid (Ni EDTA) effluent by many conventional methods. The removal of Ni(II) from Ni EDTA effluents by Fenton and Fenton-like reactions followed by hydroxide precipitation thus represents a major breakthrough (FR-HP) approach, according to Fu, Fenglian, et al. The FR-HP approach was used to investigate the kinetics of the two processes and the effectiveness of Ni(II) removal. Under optimal operating conditions, the Ni (II) removal efficiency was 92.8% and 94.7% for Fenton and Fenton-like systems, respectively, after 60 min.

Guo, Zhen-Ren, et al. [18] utilized a large amount of tannery wastewater with Chromium concentrations of 3000-6000 mg/L was generated. The major technique of recycling Chromium, sodium chloride precipitation, is substantially hampered by insufficient sludge settling. To improve precipitate sedimentation, calcium and magnesium bridging cations, as well as sonication, were used. Improvements in re-melting of Chromium sludge for usage have been made using microwave IR radiation. Over 99% of the Chromium was successfully removed from the aqueous phase by all alkalis, and 60% of it was recovered. Replacing NaOH with CaO or MgO significantly reduced sludge and shortened the settling time. MgO also improved sludge purity and dewater ability. The best alkali was a combination of CaO and MgO that balanced cost and performance. COD and SS were eliminated from the process by flushing these diment at rates of 47.6% and 86.3%, respectively. The settling of the sludge was greatly expedited by Ultrasonication at 0.12 W/cm3 for 2 minutes, cutting the settling time from 3 hours to 1 hour. The sludge's cleanliness

or particle size were not altered by sonication. The recovery of Cr increased from 60% to 80% after receiving IR microwave radiation for 5 minutes.

Mercury is of concern because it is present at low concentrations in many industrial processes and because of its tendency to bio accumulate. As accumulative toxin, the introduction of mercury into the environment can adversely affect ecosystems at all levels. So far, the rear and commercial precipitants that can irreversibly and permanently bind mercury. Blue, Lisa Y., et al. [7] test the feasibility of treating ground water in the vicinity of low-level (parts per billion, ppb) mercury chlor-alkali plants, selected commercial reagents were combined with dianionic ligands 1,3- Compared with benzene diamide ethane thiolate (BDET2-). Of all reagents tested, only K2BDET was able to reduce mercury concentrations below the instrument detection limit of 0.05 ppb, with the added advantage of producing as table precipitate.

b. Flotation

Flotation is extensively employed in today's sewage treatment process. The minerals process used flotation to remove heavy metals air bubble attachment from the liquid phase. The main flotation processes used to remove metal ions from solutions are dissolved air flotation (DAF), ion flotation, and precipitation flotation. DAF is intended to allow air micro bubbles to attach to suspended particles in water, forming less dense clusters than water. The floctorise is able to move through the water and accumulate on the surface, where it can be removed as sludge. In the 1990s, DAF was extensively researched for heavy metal removal. Table 3. Heavy metal removal by flotation summarizes the removal of heavy metals by flotation method in various studies.

Table 3: Heavy metal removal by flotation.

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Author	Heavy metal	Precipitant	Optimum pH	Initial metal concentration	Removal efficiency (%)
Aldrich, C., and D. Feng. [32]	Pb	Octa decylamine chloride	10	2 to 10 mg/L	Pb – 100 Cu – 60 Ni - 80
Blöcher, C., et al. [33]	Zn, Cu, Ni	Zeolite	8 to 10	474, 3.3, 167	-
Polat, Hurriyet, and D. Erdogan. [34]	Zn, Cu, Cr	Ethanol and methyl isobutyl carbinol	4 to 10	50 mg/L	90
Yuan, X. Z., et al. [35]	Pb, Cu, Cd	Tea saponin	6	2×10^{-5} mol/L 10^{-5} mol/L 8×10^{-5} mol/L	Cu - 81.13 Cd - 89.95 Cu - 71.17
Salmani, Mohammad Hossein, et al. [36]	Cd	Ethanol	4	-	92.1

Sourse: own elaboration.

The ability of diverse biological materials to bind metals has come to light as researchers look for novel methods to remove hazardous metals from wastewater. In order to remove heavy metals from water, a number of bio materials show promise as adsorbents. Peat moss has several benefits in these applications, including abundance, affordability, and high metal content. As a result, C. Aldrich, D. Feng, and others [11] investigated how heavy metals could be removed from aqueous solutions using sphagnum peat moss. Adsorption capacity increased with initial solution pH, and it was discovered that the adsorption process is pH dependent. A Freundlich isotherm can be used to express the sorption equilibrium. Pb>Ni>Cu>Cd was the order in which different heavy metal cations were preferred by sphagnum peat moss. The way that cations adhered to peat moss was similar to the way that they adhered to gel-like, very acidic resin.

A possible method to eliminate heavy metal ions from water-based solutions is to initially bind the metals to specially designed binders and then distinct the filled binders from the sewage stream using a separation process. Blocher, C., et al. [6] proposed a new hybrid flotation-membrane separation process was developed for the separation stage by directly incorporating a submersible microfiltration module with a specific design into the flotation reactor. As a result, it is now possible to combine the benefits of membrane separation and flotation while overcoming obstacles. A powdered synthetic zeolite was used as a binder to show that this hybrid technique is feasible. Up to 80 l.m-2.h-1 of stable flows were attained at low trans-membrane pressures using ceramic flat- film multi channel membranes. On a laboratory scale, this procedure was used to remediate effluent from the electronics sector. The base levels of Copper, Nickel, and Zinc dropped from 474, 3.3, and 167 mg/L to less than 0.05 mg/L, ensuring that emission limits were met on a consistent basis.

Polat, Hurriyet, and D. Erdogan [33] investigated heavy metal elimination from sewage which includes copper(II), zinc(II), chromium(III), and silver(I). To identify the ideal flotation conditions, a number of parameters including pH value, collector and whisk concentrations, and air throughput were examined. As collectors, Hexadecyl Trimethyl Ammonium Bromide and Sodium Dodecyl Sulphate were employed. As a whisk, ethanol and methyl isobutyl carbinol (MIBC) were utilized. Under ideal low pH circumstances, metal removal reached about 74%. It reached up to 90% at basic pH, most likely because of the involvement of suspended metal precipitates.

In order to remove Cadmium, lead, and copper from diluted aqueous solutions, Yuan, X. Z., et al. [41] studied the viability of ion flotation utilizing the herbal bio surfactant tea saponins. As demonstrated in this article, operational variables including the solution's initial pH, collector-to-heavy metal ratio, and ionic strength (NaCl) have all had an enormous effect on ions flotation efficiency. The greatest removal rates for lead, copper, and cadmium are 89.95%, 81.13%, and 71.17%, respectively, for a collector to metal ratio of 3. Tea saponins have been reported to enhance the chosen parameters of lead to Cadmium, lead to Copper, and Cadmium to Copper, with lead to Cadmium having the highest selectivity. FTIR spectroscopy was used to identify the foam products, and the results showed that the carboxylate groups and divalent metal ions that were present in the entire solution generated distinct complexes.

"Ion flotation" is a separation process that has lately experienced a surge in research effort. This technique offers four significant advantages for wastewater treatment. Low energy usage, small area requirements, low sludge quantity, and timely effect. Salmani, Mohammad Hossein et al. [35] targeted for optimal ion flotation variables for Cadmium expulsion in replicated sewage on an industrial magnitude. It was developed by reacting Cd2+ with a Sodium Dodecyl Sulphate (SDS) collector and then gliding it in ethanol as a whisk. Test solutions were made by adding the necessary amounts of Cadmium ions, SDS, and foam or Sodium Sulphate solution. All tests were conducted on flotation columns for 120 minutes at laboratory temperature (27°C) and pH=4. The flotation process is influenced by rate of flow, Cadmium, SDS, blend concentration, and ionic strength. At a flow rate of 150 mL/min and a collector to metal ratio of 3.1, the highest achievable separation efficiency was 84% after

60 minutes. According to similar conditions, 0.4% ethanol was infused to the flotation tower and the highest percentage of cadmium removal was 92.1%. Cadmium and collectors seemed productively abolished from the sewage, in line with the results obtained. As an outcome, there's evidence that using ion flotation to get rid of metal ions from effluent is efficient.

c. Ion exchange

The ion exchange method is often employed to get rid of heavy metals from sewage due to its multiple benefits, including high productivity, high efficacy in removal, and rapid acceleration. Ion exchange resins, either natural or synthetic, are distinctive in their ability to transform cations for metals in sewage. Since synthetic resins are quite efficient at eliminate heavy metals from solutions, they have a widespread application in ion exchange methods. Table 4 summarizes current attempts to remove heavy metals through ion exchange.

Author	Heavy metal	Resin	Optimum pH	Initial metal concentration	Removal efficiency (%)
Oehmen, Adrian, et al. [37]	As, Hg	-	-	-	98.56
Lee, I-Hsien,et al. [38]	CD, Cu, Zn	Amberlite IR-	-	-	-
Badawy, N. A., et al. [39]	Pb	Purolite C100	-	-	99.17
Shaidan, Nur Hamizah,et al. [40]	Ni	Acidic cation exchange resin	3 to 7		97
Carro, Leticia, et al. [41]	Cd, Pb	Sargassummuticum loaded with calcium	5	0.1 to 6 mmol/L	-
Thakare, Yogeshwar N.,et al. [42]	Cu	Indion 225H	6.3 to 6.5	50 to 150 mg/L	-
Zewail, T. M., and N. S. Yousef. [43]	Pb, Ni	Amberjet 1200 Na	-	1800 mg/L, 2800 mg/L, 3800 mg/L	98, 99

Sourse: own elaboration.

According to Oehmen, Adrian et al. [31] Arsenic (As) and mercury (Hg) are two incredibly harmful metals which needs to be eradicated from sources of water for consumption at levels that are extremely low. The ion-exchange membrane bioreactor (IEMB) technology is a novel approach for removing both chemicals. Donnan dialysis transports impurities across ion-exchange membranes, followed by biological elimination of contaminants. The IEMB method, as reported in this article, is likely to be utilized in drinking water treatment systems and offers a number of advantages over already deployed techniques, including reducing the danger of drinking water cross-contamination.

Ion exchange holds an enormous amount of potential to eliminate heavy metals from wastewater from industries and sludge. To develop and run a heavy metal removal process, it is crucial to first understand the equilibrium connection between ions and resins. As a result, Lee, I-Hsien, and colleagues [22] employed the Amberlite IR-120 to conduct a series of ion-exchange equilibrium studies for Cu2+/H+, Zn2+/H+, and Cd2+/H+ systems. The Langmuir isotherm, Freundlich isotherm, and electivity factor techniques were used to analyse equilibrium data. Gibbs energy change, enthalpy change, and entropy change were determined as thermodynamic parameters. When the selectivity coefficients are compared, the affinity sequence for IR-120 is Cu2+>Zn2+>Cd2+>H+. Ion exchange kinetics were further investigated in order to comprehend heavy metal extraction kinetics in the presence of Amberlite IR-120. Pseudo-models of first-order, second-order, and reversible reaction models have been utilized for regression analysis of the ion-exchange kinetic data. At numerous temperatures, the triggering energies calculated from the rate indices are 15.41, 7.04, and 17.01 kJ/mol for copper, zinc, and cadmium respectively. Though first- and second-order pseudo models tend to be more convenient for examining data, the model parameters they provide are dependent on the circumstances of operation. The consequences of resin-to-solution ratio, initial heavy metal concentration, and temperature on onion-exchange kinetic curves can be estimated using reversible reaction models.

Badawy. N. A., et al. [5] demonstrated a straightforward solid-phase extraction approach utilising Purolite C100 cation exchange resin. This method uses column technology to separate and recover lead ions from synthetic binary mixtures. The equilibrium partition coefficients kd of several metal ions, including Al(III), Fe(III), Ba(II), and Pb(II), were determined at 25° C in the presence of variable quantities of nitric acid and ammonium acetate solutions. The value of the separation factor was computed. Because ammonium acetate is a good eluent for lead ions but not for other cations, quantitative separation of lead ions from synthetic binary combinations is based on this property.

Ion exchange is a powerful method for eliminating heavy metals from wastewater. A small number of studies have been conducted to assess the performance of fixed beds for metal removal. Shaidan, Nur Hamizah, and colleagues [37] examined the removal of Ni2+ from synthetic wastewater in a packed bed column employing a very acidic cation exchange resin. Experiments were carried out at pH levels ranging from 3 to 7 with starting heavy metal concentrations of 1.8, 2.8, and 3.8g Ni/L. The influence of resin production was examined. A kinetic study of the process was done, and break through curves were employed to demonstrate the scavenging efficiency and rate. We monitor the exchange dynamics using the Thomas model and compare the experimental findings to the Thomas model results, indicating that the estimated break through curves agree well with the measure dones. An atomic absorption spectrophotometer was used to evaluate the metal content of the treated wastewater, which demonstrated that the Ni2+ concentration was below acceptable environmental limits.

The exchange mechanisms that occur during the removal process of various metallic cations by natural biomass were analyzed using the calcium-loaded brown algae Sargassummticum. Sorption experiments and kinetic studies with varying initial metal concentrations were performed. Carro, Leticia, et al. [8] conducted experiments with Cadmium and lead and observed a one to one correlation across the amount of metal exchanged by a substance as well as the quantity of calcium released into solution. Across all metal concentrations, this ratio remained consistent. This finding led to the conclusion that cadmium removal by brown algae is mostly related to exchange activities with calcium cations that are still present in the material structure. According to the kinetic data, the rate-limiting stage in the Cadmium removal process is film diffusion. In contrast, investigations with mercury revealed different proportions based upon metal existence, resulting in greater mercury getting eliminated from solution than calcium being re-released. When the results for mercury are compared to those for Cadmium, it may be assumed that mercury removal includes not just an exchange process, but also a reduction mechanism. For the first time, SEM and EDS analyses demonstrated mercury reduction following batch sorption studies.

In sewage treatment, high density ion exchange resins are utilized to get rid of trace metals and are ideal for adsorptive separation in enlarged beds. Thakare, Yogeshwar N., et al. [40] chose the synthetic cation exchange resin INDION225H for a deeper knowledge of such adsorbents. SEM-EDS and FTIR are used to evaluate the physical characteristics of various sorbents. Cu(II) is employed as an adsorption model solvent. Adsorption equilibrium investigations are carried out, as well as the estimation of isotherm parameters. Adsorption kinetics for feed concentrations ranging from 50 to 150 mg/L, as well as thermodynamics at temperatures ranging from 20°C to 60°C, were investigated across a pH range of 6.3 to 6.5. Copper ion adsorption on INDION 225H follows two isotherms, the Freundlich isotherm and the Redrich-Peterson isotherm, showing multi-layer adsorption, according to the current work. Adsorption energies in the chemi-sorption range were identified.

An entrained bed contactor is a cross between a fixed bed contactor and a fluidized bed contactor that retains the advantages of both while preserving acceptable hydrodynamic conditions. The effectiveness of an inconsistent cylindrical air-jet tank for heavy metal elimination through an effective cations-exchange resin (AMBERJET 1200Na) is investigated by Zewail, T. M., and N. S. Yousef [42]. The implications of heavy metal ion forms (Ni+2 and Pb+2), time of contact, surface air velocity, and heavy metal initial ion concentration on the elimination rate of heavy metal ions have been examined. Within the ideal circumstances, 98% and 99% elimination of Ni+2 and Pb+2 was achieved respectively. Multiple kinetic models were employed to validate the outcomes of experiments alongside examine the underlying mechanisms of adsorption process control. The present Ni+2 and Pb+2 data are well matched to second-order dynamics pseudo models with strong correlation coefficients. The ion exchange mechanism is aided by both membrane diffusion and intra particle diffusion. This study shown that the spout bed vessel might be a viable option for producing ion-exchange processes.

III. REMARKS OF HEAVY METAL TREATMENT METHODS

Operating expenses, starting metal ion concentration, environmental effect, pH, extra chemicals, removal efficiency, and economics all play a role in determining the best technique for removing heavy ions from wastewater. Several significant variables are at work. These techniques include adsorption (using various adsorbents including carbon-based, carbon composites, mineral, CS, magnetic, bio sorbents, and MOFs) and membrane processes (such as UF, Nano filtration, microfiltration, reverse osmosis, forward osmosis, and electro dialysis). Chemical processes (such as chemical precipitation, flotation, and ion exchange). Due to its ease of use, adaptability, high elimination rate, and low reliability, adsorption is the most ensuring and most researched method for elimination of heavy metal complexes from wastewater. This priority, however, is mostly dependent on low-cost material selection, high uptake, and effective regeneration processes. Compared to adsorption, membrane processes are more practical and therefore technologically mature. However, minimizing separation costs and membrane fouling remains a challenge. Chemical processes, particularly chemical precipitation, are technically mature and practicable. It is also regarded as a low-cost approach. In contrast to electrochemical processes, which are dependent on extra elements such as electrodes, power, and other fixed expenses, they are dependent on the chemicals consumed. However, a substantial volume of sludge is produced, necessitating sedimentation separation. The electrochemical technique is rather costly technique due to electrode passivation and high power consumption. In addition, electrical processes are the least mature technologies alongside photo catalytic processes. The advantages of the photo catalytic process are that it uses no (or less) chemicals, produces less sludge and is environmentally friendly. In general, the most practicable methods mentioned in the literature are chemical, adsorption, and membrane approaches. Most of the studies used synthetic wastewaters in which one or more metal species were present, indicating there is a significant information gap in the performance of treatment strategies for eliminating heavy metal ions from actual wastewaters. Therefore, more research needs to be done to treat different contaminants in real waste. Further research is needed to introduce cost-effective materials and methods to remove heavy metals from waste. Future research should also concentrate on small-scale processes. The most effective methods to reduce environmental impact and achieve cost-effective and efficient metal recovery are still under development and should be considered in future studies.

IV. CONCLUSION

The most serious environmental concern in the world is dangerous heavy metal poisoning of wastewater. Chemical precipitation, coagulation, floculation, flotation, ion exchange, and membrane filtering are heavy metal removal procedures used to meet increasingly demanding environmental criteria. This is evident from a review of various studies on ion exchange, adsorption, and membranes. For severe metal wastewater treatment, filtration is the most investigated method. Metals are removed from wastewater via ion exchange methods, which are commonly employed. Low-cost adsorption Adsorbents and bio-sorbents are thought to be useful in the treatment of wastewater with low heavy metal concentrations. AC is seen as a backup. Membrane filtration is a type of filtering technology. Heavy metal ions are efficiently removed. When contemplating heavy metal removal, actual sewage should be used rather than synthetic sewage.

V. REFERENCES

- [1] Aldrich, C., and D. Feng. "Removal of heavy metals from wastewater effluents by biosorptive flotation". Minerals engineering 13.10-11 (2000): 1129-1138.
- [2] Alvarez, Maria Teresa, Carla Crespo, and Bo Mattiasson. "Precipitation of Zn(II), Cu(II) and Pb (II) at bench-scale using biogenic hydrogen sulfide from the utilization of volatile fatty acids". Chemosphere 66.9 (2007): 1677-1683.
- [3] Azabou, Samia, TaharMechichi, and Sami Sayadi. "Zinc precipitation by heavy-metal tolerant sulfate-reducing bacteria enriched on phosphogypsum as a sulfate source". Minerals Engineering 20.2 (2007): 173-178.
- [4] Azanaw, Aklilu, et al. "Textile effluent treatment methods and eco-friendly resolution of textile wastewater". Case Studies in Chemical and Environmental Engineering (2022): 100230.
- [5] Badawy, N. A., et al. "Chromatographic separations and recovery of lead ions from a synthetic binary mixtures of some heavy metal using cation exchange resin". Journal of hazardous materials 166.2-3 (2009): 1266-1271.
- [6] Blocher, C., et al. "Hybrid flotation-membrane filtration process for the removal of heavy metal ions from wastewater". Water Research 37.16 (2003): 4018-4026.
- [7] Blue, Lisa Y., et al. "Low-level mercury removal from groundwater using a synthetic chelating ligand". Water research 42.8-9 (2008): 2025-2028.

- [8] Carro, Leticia, et al". Interaction of heavy metals with Ca-pretreated Sargassummuticum algal biomass: Characterization as a cation exchange process". Chemical Engineering Journal 264 (2015): 181-187.
- [9] Chen, Quanyuan, et al. "Precipitation of heavy metals from wastewater using simulated flue gas: sequent additions of fly ash, lime and carbon dioxide". Water research 43.10 (2009): 2605-2614.
- [10] Chowdhary, Pankaj, et al. "Role of industries in water scarcity and its adverse effects on environment and human health". Environmental concerns and sustainable development. Springer, Singapore, 2020. 235-256.
- [11] Chowdhary, Pankaj, et al. "Role of industries in water scarcity and its adverse effects on environment and human health". Environmental concerns and sustainable development. Springer, Singapore, 2020. 235-256.
- [12] Crini, Grégorio, and Eric Lichtfouse. "Advantages and disadvantages of techniques used for wastewater treatment". Environmental Chemistry Letters 17.1 (2019): 145-155.
- [13] Date, Manali, et al. "Zero liquid discharge technology for recovery, reuse, and reclamation of wastewater: A critical review". Journal of Water Process Engineering 49 (2022): 103129.
- [14] Dhaliwal, Salwinder Singh, et al. "Remediation techniques for removal of heavy metals from the soil contaminated through different sources: a review". Environmental Science and Pollution Research 27.2 (2020): 1319-1333.
- [15] Fu, Fenglian, et al. "Application of a novel strategy—Advanced Fenton-chemical precipitation to the treatment of strong stability chelated heavy metal containing wastewater". Chemical Engineering Journal 189 (2012): 283-287.
- [16] Fu, Fenglian, et al. "Effective removal of coordinated Copper from wastewater using a new dithio carbamate-type supra molecular heavy metal precipitant". Chemosphere 69.11 (2007): 1783-1789.
- [17] Fu, Fenglian, Qi Wang, and Bing Tang. "Fenton and Fenton-like reaction followed by hydroxide precipitation in the removal of Ni (II) from Ni EDTA wastewater: a comparative study". Chemical Engineering Journal 155.3 (2009): 769-774.
- [18] Guo, Zhen-Ren, et al. "Enhanced Chromium recovery from tanning wastewater". Journal of Cleaner Production 14.1 (2006): 75-79.
- [19] Gyamfi, Ebenezer, Emmanuel Kwame Appiah-Adjei, and Kwaku Amaning Adjei. "Potential heavy metal pollution of soil and water resources from artisanal mining in Kokoteasua, Ghana". Groundwater for Sustainable Development 8 (2019): 450-456.
- [20] Jiang, Chun-yu, et al. "Isolation and characterization of a heavy metal-resistant Burkholderia sp. from heavy metal-contaminated paddy field soil and its potential in promoting plant growth and heavy metal accumulation in metal-polluted soil". Chemosphere 72.2 (2008): 157-164
- [21] Kumar, Sandeep, et al. "Hazardous heavy metals contamination of vegetables and food chain: Role of sustainable remediation approaches-A review". Environmental research 179 (2019): 108792.
- [22] Lee, I-Hsien, Yu-Chung Kuan, and Jia-Ming Chern. "Equilibrium and kinetics of heavy metal ion exchange". Journal of the Chinese Institute of Chemical Engineers 38.1 (2007): 71-84.
- [23] Maity, Sourav, Debopriya Sinha, and Angana Sarkar. "Wastewater and industrial effluent treatment by using nanotechnology". Nano materials and Environmental Biotechnology. Springer, Cham, 2020. 299-313.
- [24] Matlock, Matthew M., Brock S. Howerton, and David A. Atwood. "Chemical precipitation of heavy metals from acid mine drainage". Water research 36.19 (2002): 4757-4764.
- [25] Matlock, Matthew M., et al. "A pyridine-thiol ligand with multiple bonding sites for heavy metal precipitation". Journal of Hazardous Materials 82.1 (2001): 55-63.
- [26] Mauchauffée, Stephanie, and Eric Meux. "Use of Sodium decanoate for selective precipitation of metals contained in industrial wastewater". Chemosphere 69.5 (2007): 763-768.
- [27] Mirbagheri, S. Ahmad, and Seyed Nezamedin Hosseini. "Pilot plant investigation on petrochemical wastewater treatment for the removal of Copper and Chromium with the objective of reuse". Desalination 171.1 (2005): 85-93.
- [28] Mishra, Sandhya, et al. "Heavy metal contamination: an alarming threat to environment and human health". Environmental biotechnology: For sustainable future. Springer, Singapore, 2019. 103-125.
- [29] Muhammad, Said, and Kashif Ahmad. "Heavy metal contamination in water and fish of the Hunza River and its tributaries in Gilgit—Baltistan: evaluation of potential risks and provenance". Environmental technology & innovation 20 (2020): 101159.
- [30] Nigam, Adarsh, et al. "Development of semiconductor based heavy metal ion sensors for water analysis: A review". Sensors and Actuators A: Physical 330 (2021): 112879.
- [31] Oehmen, Adrian, et al. "Removal of heavy metals from drinking water supplies through the ion exchange membrane bioreactor". Desalination 199.1-3 (2006): 405-407.
- [32] Pandiyan, Jeganathan, et al. "An assessment of level of heavy metals pollution in the water, sediment and aquatic organisms: A perspective of tackling environmental threats for food security". Saudi Journal of Biological Sciences 28.2 (2021): 1218-1225.
- [33] Polat, Hurriyet, and D. Erdogan. "Heavy metal removal from waste waters by ion flotation". Journal of Hazardous Materials 148.1-2 (2007): 267-273.
- [34] Rahman, Zeeshanur, and Ved Pal Singh. "The relative impact of toxic heavy metals (THMs)(arsenic (As), Cadmium (Cd), Chromium (Cr)(VI), mercury (Hg), and lead (Pb)) on the total environment: an overview". Environmental monitoring and assessment 191.7 (2019): 1-21.
- [35] Salmani, Mohammad Hossein, et al. "Removal of Cadmium (II) from simulated wastewater by ion flotation technique". Iranian Journal of Environmental Health Science and Engineering 10.1 (2013): 1-5.
- [36] Sarode, Shruti, et al. "Overview of wastewater treatment methods with special focus on biopolymer chitin-chitosan". International journal of biological macromolecules 121 (2019): 1086-1100.
- [37] Shaidan, NurHamizah, UsamaEldemerdash, and SherineAwad. "Removal of Ni (II) ions from aqueous solutions using fixed-bed ion exchange column technique". Journal of the Taiwan Institute of Chemical Engineers 43.1 (2012): 40-45.
- [38] Shih, Yu-Jen, Chih-Ping Lin, and Yao-Hui Huang. "Application of Fered-Fenton and chemical precipitation process for the treatment of electroless nickel plating wastewater". Separation and Purification Technology 104 (2013): 100-105.
- [39] Singh, Ajay. "A review of wastewater irrigation: Environmental implications". Resources, Conservation and Recycling 168 (2021): 105454.
- [40] Thakare, Yogeshwar N., and Arun Kumar Jana. "Performance of high density ion exchange resin (INDION225H) for removal of Cu (II) from waste water." Journal of Environmental Chemical Engineering 3.2 (2015): 1393-1398.
- [41] Yuan, X. Z., et al. "Evaluation of tea-derived biosurfactant on removing heavy metal ions from dilute wastewater by ion flotation". Colloids and Surfaces A: Physicochemical and Engineering Aspects 317.1-3 (2008): 256-261.

- [42] Zewail, T. M., and N. S. Yousef. "Kinetic study of heavy metal ions removal by ion exchange in batch conical air spouted bed". Alexandria Engineering Journal 54.1 (2015): 83-90.
- [43] Zuo, Wenchao, Yueqing Li, and Yuhong Wang. "Research on the optimization of new energy vehicle industry research and development subsidy about generic technology based on the three-way decisions". Journal of Cleaner Production 212 (2019): 46-55.
- [44] Vayampully Ajitha, Jordan Jun Chul Park et al. "Current physicochemical treatment technologies available for remediation of different types of heavy metals from wastewater". New Trends in Removal of Heavy Metals from Industrial Wastewater-Book chapter 12 (2021): 301-322.