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Review Article

Efficient Removal of Heavy metals from Oil-field Produced Water: A Review of Currently Available Techniques

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Abstract

Oil and gas production operations from depleted oil and gas fields often result in the production of enormous amount of water. Even though, disposal of this oil-field produced water itself is a challenging task, however at the same time, treated oil-field produced water can provide an unconventional source of water that could be used for certain beneficial reuses.

The present study reports on the review of various currently available oil-field water treatment technologies with a focus on heavy metals removal technologies. It appears that the photo catalytic methods are the most promising methods for removing heavy metals from oil-field produced water. However, several factors including the initial metal concentration, the component of the wastewater, capital investment and operational cost, plant flexibility and reliability, environmental impact, and utility of the treated water have a great influence on the selection of the most suitable treatment techniques.

Introduction

Extraction of oil and gas from underground reservoirs often is accompanied by water or brine, which is referred to as produced water. Produced water is the largest waste-stream of oil and gas exploration which includes water trapped in underground formations and water injected into the stratum to drive out the crude oil [1]. In early stages of oil production, water content is usually low but can rise to as high as 80% during the later years of the well [2]. As reservoirs mature, especially if secondary or tertiary recovery methods are used, the quantity of water climbs and often exceeds the volume of the hydrocarbons before the reservoir is exhausted. It has been observed that in some of the oil-fields this ratio is 1:15 where 15 parts of water accompany just 1 part of oil. Global produced water production is estimated at about 250 million barrels per day compared with about 80 million barrels per day of oil [3]. The chemical composition and behaviour of produced water varies when compared with the surface waters because they are constrained within an aquifer and has distinctive characteristics due to the presence of organic and inorganic matters, high salinity, BTEX, PAH, heavy metals etc. which can cause toxicity to the environment [4]. Generally, produced water is composed of dissolved and dispersed oil components, dissolved formation minerals, production chemicals, dissolved gases (including CO_2 and H2S) and produced solids. There is a wide variation in the level of its organic and inorganic composition due to geological formation, lifetime of the reservoir and the type of hydrocarbon produced. Also, this produced water contains various microorganisms which result in microbial corrosion of the inner surfaces of pipes by forming bio films on the metal surfaces [5]. The constituents of produced water vary and can differ from well to well with pH in the range of 6-8.5 [6]. Produced water is increasingly being considered to supplement limited freshwater resources in many parts of the US as well as other countries [7]. The cost of producing, handling, and disposing of the produced water often defines the economic lifetime of a field and the actual hydrocarbon reserves; therefore, understanding and predicting the aspects, behaviour, and problems induced by the produced-water flow is important.

Composition of oil-field produced water

Oil field produced water generally consists of dispersed and dissolved oil components those are mixture of hydrocarbons including BTEX (benzene, toluene, ethylbenzene and xylene), PAHs (polyaromatic hydrocarbons) and phenols. Dissolved oils are the polar constituent organic compounds in produced water, while small droplets of oil suspended in the aqueous phase are called dispersed oil [8-10]. BTEX, phenols, aliphatic hydrocarbons, carboxylic acid and low molecular weight aromatic compound are classified as dissolved oil, while less-soluble PAHs and heavy alkyl phenols are present in produced water as dispersed oil [11]. Dissolved and dispersed oil has to be removed in order to utilize this produced water for some efficient reuse.

Dissolved inorganic compounds or minerals are usually high in concentration, and classified as cations and anions, naturally occurring radioactive materials and heavy metals. Cations and anions play a significant role in the chemistry of produced water. Na and Cl_2 are responsible for salinity, ranging from a few milligrams per litre to 300000 mg/L [12]. Cl_2, SO_4, CO_3, HCO, Na, K, Ca_2, Ba_2, Mg_2, Fe_2 and Sr_2 affect conductivity and scale-forming potential. Typical oilfield produced water contains heavy metals in varied concentrations, depending on the formation geology and the age of oil well and its concentration is usually higher than those of receiving water (for enhanced oil recovery) and those found in sea water[13]. 226Ra and 228Ra are the most abundant naturally occurring radioactive elements present sometimes in oilfield produced water [13]. Radioactivity of produced water results primarily from radium that is co-precipitated with barium sulphate (scale) or other types of scales [14].

Current scenario of oil-field produced water disposal

At present, oil and gas operators manage the produced water by following one or more of the options. Some try to avoid production of water by blocking the water fractures by polymer gel or down hole water separator; but this option is not always possible as water would generally be produced during secondary and tertiary extraction process of oil. Another is injecting the produced water back into the formations. However, this demands transportation of water, and treatment to reduce fouling and bacterial growth. In the long term, the stored produced water may pollute the underground waters. Also, some follows its discharge in to the environment if it meets onshore and offshore discharge regulations. Petroleum industry may try reusing minimally treated produced water for drilling and work over operations. Finally, it could be utilized for beneficial domestic purposes such as for irrigation, wildlife consumption and industrial water, but this may involve significant treatment [3,15].

Environmental concerns and the prospect of beneficial uses have driven research into the treatment of produced water. Current conventional treatment technologies are targeted at removal of heavy metals, oil and grease, suspended solids, and desalination, which often lead to the generation of large volumes of secondary waste. For instance, heavy metals are removed as sludge using current treatment technologies [16]. This article reviews current produced water efficient, eco-friendly and cost effective treatment technologies for removal of heavy metals thereby rendering the produced water for reuse with minimal negative impact on the environment.

Pre-treatment methods for oil-field produced waters

The first pre-treatment process of the oil-field produced waters containing traces of oil is the oil-water separation. The conventional rectangular-channel separators, developed by the American Petroleum Institute (API) are wildly used for this purpose, and their design criteria are summarized in the publication API, 1990 [17]. Many other separators had been developed based on the oil-water separation theory and some of them, as the parallel plate and corrugated plate separators, had been implemented in the petroleum refineries [18]. The oil separators remove only the fraction of free oil, whereas the emulsified and the dissolved oil remain in the separator effluent in the form of oil-water emulsions. These emulsions could be destabilized using chemical de stabilizers followed by separation using dissolved air flotation technique (DAF) [19-21]. Different biological treatment processes that have been utilized for treating produced water are aerated ponds, activated sludge, biological contactors, sequential bath reactors and moving bed reactors [22-25]. Initial researches that had been done for recycling of the biologically treated refinery effluent involved the use of activated carbon adsorption alone or in combination with ozonation or sand filtration [26-28]. The membrane technology development allowed additional options, such as ultrafiltration and reverse osmosis [29-32].The implementation of the advanced treatment technology allowed reusing of the biologically treated wastewater and freshwater savings in the refineries.

Effects of heavy metals

Heavy metals are generally considered to be those whose density exceeds 5 g per cubic centimetre and atomic weights between 63.5 and 200.6. Most heavy metals are well-known toxic and carcinogenic agents and it represent a serious threat to the human population and the fauna and flora of the receiving water bodies. Heavy metals have a great tendency to bio-accumulate and end up as permanent additions to the environment and have detrimental effect on human health [33]. Once they enter the food chain, large concentrations of heavy metals may accumulate in the human body. If the metals concentrations are ingested beyond the permitted value, they can cause serious health disorders. A large number of elements fall into this category, but the ones discussed here are those of relevance in the environmental context. Arsenic is usually regarded as a hazardous heavy metal even though it is actually a semi-metal. Heavy metals cause serious health effects, including reduced growth and development, cancer ,organ damage, nervous system damage, and in extreme cases, death. Exposure to some metals, such as mercury and lead, may also cause development of autoimmunity, in which a person's immune system attacks its own cells. This can lead to joint diseases such as rheumatoid arthritis, and diseases of the kidneys, circulatory system, nervous system, and damaging of foetus's brain. Wastewater regulations were established to minimize human and environmental exposure to hazardous chemicals. This includes limits on the types and concentration of heavy metals that may be present in the discharged wastewater [34-35].

Produced water management techniques

The general objectives for operators treating produced water are: de-oiling (removal of dispersed oil and grease), desalination, removal of suspended particles (salts) and sand, removal of soluble organics, removal of dissolved gases, removing traces of heavy metals, removal of naturally occurring radioactive materials (NORM), disinfection and softening (to remove excess water hardness) [15]. In this current review, different methods to remove heavy metals from oil-field produced waters have been discussed in detail. These methods include chemical precipitation, coagulation, flocculation, ion-exchange, adsorption, membrane filtration, Reverse Osmosis, floatation, electrochemical treatment technologies, Electro dialysis, Photo catalysis and biological methods.

Chemical Precipitation, Coagulation and Flocculation

The conventional method for heavy metal removal from industrial wastewater generally involves a chemical precipitation process [36-39].Of the various treatment methods employed to remove heavy metals, hydroxide precipitation is the most common treatment technology. Heavy metals are removed by adding alkali such as caustic, lime or soda ash to adjust the wastewater pH to the point where the metals exhibit a minimum solubility. Then a proper solid-liquid separation technique removes the metal precipitation such as sedimentation and filtration. The conventional heavy metal removal process has some inherent short comings such as requiring a large area of land, a sludge dewatering facility, skilful operators and multiple basin configurations [40]. The conceptual mechanism of heavy metal removal by chemical precipitation is presented in Eq. (1) $M^{2+} + 2(OH)- \leftrightarrow M(OH)_2$, [41].

Where, M^{2+} and OH represent the dissolved metal ions and the precipitant, respectively, while $M\,(OH)_2$ is the insoluble metal hydroxide. Adjustment of pH to the basic conditions (pH range of 9–11) is the major parameter that significantly improves heavy metal removal by chemical precipitation. Lime and limestone are the most commonly employed precipitant agents due to their availability and low-cost in most countries [42- 43]. Lime precipitation can be employed to effectively treat inorganic effluent with a metal concentration of higher than 1000 mg/L and other advantages of using lime precipitation include the simplicity of the process, inexpensive equipment requirement, and convenient and safe operations. To enhance lime precipitation, fly ash was used as a seed material [43]. The fly ash- lime carbonation treatment increased the particle size of the precipitate and improved the efficiency of heavy metal removal. In hydroxide precipitation process, the addition of coagulants such as alum, iron salts, and organic polymers can enhance the removal of heavy metals from wastewater Another researcher employed chemical coagulation and precipitation by lime to treat synthetic wastewater [44]. Sulphide precipitation is also an effective process for the treatment of toxic heavy metal ions. One of the primary advantages of using sulphides is that the solubility's of the metal sulphide precipitates are dramatically lower than hydroxide precipitates and sulphide precipitates are not amphoteric. Also, this process can achieve a high degree of metal removal over a broad pH range compared with hydroxide precipitation. Metal sulphide sludge also exhibit better thickening and de watering characteristics than the corresponding metal hydroxide sludge. However, there are potential dangers in the use of sulphide precipitation process as it many times results into evolution of toxic H2S fumes. However, chemical precipitation has been successful in combination with other methods and a reported literature shows that sulphide precipitation can reuse and recover heavy metalions by employing nano filtration as a second step [45]. There are some reports on chemical precipitation in combination with ion-exchange treatments. Here nickel was removed with the help of ion-exchange in combination of chemical precipitation [46].Another novel method is nucleation precipitation which is a simple cost effective method to strip off heavy metals in a fluidized sand bed. In operation, the metal-bearing wastewater is pumped through a fluidized sand column with a simultaneous injection of carbonate solution to raise pH metal precipitation to occur and then deposit on the sand surface (nucleated precipitation) rather than to form discrete metal original sand grains are 0.2-0.3mm in diameter, but quickly grow to a much larger size (up to 2 or 3mm) upon continuous coating of metal precipitates. The larger coated sand particles sink to the bed bottom from which they can be easily removed and new sand can then be added from the top of the stripper. Since the coated particle contains a high level of metal mineral, they can be collected for mineral recovery [47]. However, chemical precipitation requires large amounts of chemicals to reduce metals to an acceptable level for discharge along with excessive sludge formation that requires further treatment, slow metal precipitation, poor settling, the aggregation of metal precipitates, and the long-term environmental impacts of sludge disposal [48]. Coagulation is one of the most important methods for wastewater treatment, but the main objects of coagulation are only the Hydrophobic colloids and suspended particles. Flocculation is the action of polymers to form bridges between the flocs and bind the particles into large agglomerates or clumps. Once suspended particles are flocculated into larger particles, they can usually be removed or separated by filtration, straining or floatation. Today many kinds of flocculants, such as PAC, poly ferric sulphate (PFS) and poly acryl amide (PAM), are widely used in the treatment of wastewater; however, it is nearly impracticable to remove heavy metal very well from wastewater directly by these current flocculants.

Ion-Exchange Method

Ion exchange may be defined as the exchange of ions between the substrate and surrounding medium. The most useful ion exchange reaction is reversible, whereby the reaction is reversible and the ion exchanger can be regenerated and reused many times. Generally, resins are manufactured in the spherical, stress and strain free form to resist physical degradation. They are stable at high temperatures and applicable over a wide pH range. Ion exchange resins, which are completely insoluble in most aqueous and organic solutions, consist of across linked polymer matrix to which charged functional groups are attached by covalent bonds [49]. Typical ion exchangers are produced with a particle size distribution in the range 20-50mesh (for separation of anions from cations or of ionic species from non ionic ones). For more difficult separations, materials of smaller particle size or lower degrees of cross linking are necessary. Depending on the type of functional groups of exchanging certain ions, the ion exchangers with strongly acidic e.g., sulphonate $-SO_3H$, weakly acidic e.g, carboxylate -COOH, strongly basic e.g., quaternary ammonium $-N+R_3$ and weakly basic e.g., tertiary, and secondary amine-$N+R_2H$ and $-N+RH_2$ should be mentioned. The strong acidic cation exchangers are well dissociated over a wide pH range and thus reaching its maximum sorption capacity. There are also amphoteric exchangers, which depending on the pH of the solution may exchange either cations or anions. More recently these ion exchangers are called bipolar electrolyte exchange resins (BEE) or zwitter ionic ion exchangers [50].

Ion-exchange processes have been widely used to remove heavy metals from oil-field produced water and other waste waters due to advantages such as high treatment capacity, high removal efficiency and fast kinetics [51]. Ion-exchange resin, either synthetic or natural solid resin, has the specific ability to exchange its cations with the metals in the wastewater; however, synthetic resins are commonly preferred as they are effective to nearly remove the heavy metals from the solution [52]. Hydrogen ions in the sulfonic group or carboxylic group of the resin can serve as exchangeable ions with metal cations. The uptake of heavy metal ions by ion-exchange resins is rather affected by certain variables such as pH, temperature, initial metal concentration and contact time [53]. Ionic charge also plays an important role in ion-exchange process which could be incurred from the study of removal of Ce_4, Fe_3 and Pb_2 from aqueous systems by cation-exchange resin purolite C100 [54]. Similar results for Co_2, Ni_2 and Cr_3 in an Amber lite IRN-77 cation exchange resin were previously obtained [55].

Besides synthetic resins, natural zeo lites, naturally occurrings ilicate minerals, have been widely used to remove heavy metal from aqueous solutions due to their low cost and high abundance. Many researchers have validated that zeolites exhibit good cation-exchange capacities for heavy metal ions under different experimental conditions [56]. Clinoptilolite is one of the most frequently studied natural zeolites that have received extensive attention due to its selectivity for heavy metals. It has been studied that the surface of clinoptilolite loaded with amorphous Fe-oxide species would significantly improve its ion-exchange capacity [57]. Doula [57] employed clinoptilolite-Fe system to simultaneously remove Cu, Mn and Zn from drinking water and found that the system has very large metal adsorption capacity and for most of the cases the treated water samples were suitable for human consumption or agricultural use [58].

Adsorption Method

Adsorption is now recognized as an effective and economic method for heavy metal wastewater treatment. The adsorption process offers flexibility in design and operation along with producing high-quality treated effluent. It is also very efficient because adsorption is sometimes reversible, adsorbents can be regenerated by suitable desorption process [59]. In recent years, the search for low cost adsorbents that have metal-binding capacities has been investigated [60]. The adsorbents may be of mineral, organic or biological origins, zeolites, industrial by-products, agricultural wastes, biomass, and polymeric materials [61]. Various other effective adsorbents are activated carbon, carbon nanotubes, low-cost adsorbents, bio adsorbents [59]. There are many adsorbents that can be used for the removal of metal ions from wastewater and, certainly, cost plays an important role for determining which one is applicable. Activated carbon (AC) adsorbents are widely used in the removal of heavy metal contaminants due to its large micro pore and meso pore volumes and the resulting high surface area. A large number of researchers are studying the use of AC for removing heavy metals [62].

Nowadays, the depleted source of commercial coal-based AC has resulted into increase in its price thereby opting other additives along with AC such as alginate, tannic acid and magnesium [63-65]. Converting carbonaceous materials into AC for heavy metals remediation have been reported. The use of AC from eucalyptus bark in the binary component sorption of Cu2 and Pb2and poultry litter to manufacture AC for treating heavy metal-contaminated water was explored [66-67]. Carbon nanotubes (CNTs) discovered by Iijima [68], have been widely studied for their excellent properties and applications as new adsorbents possessing great potential for removing heavy metal ions such as lead [69], cadmium [70], chromium [71], copper and nickel [72] from waste water. CNTs are divided into two types: (1) single-walled CNTs (SWCNTs) and (2) multi-walled CNTs (MWCNTs) [73]. The mechanisms by which the metal ions are adsorbed onto CNTs are very complicated and appear attributable to electrostatic attraction, sorption-precipitation and chemical interaction between the metal ions and the surface functional groups of CNTs [74]. The sorption capacities of metal ions by raw CNTs are very low but significantly increase after oxidized by HNO_3, NaClO and $KMnO_4$ solutions.

Despite these recently developed adsorbents the search for low cost and easily available adsorbents has become main research focus today. Studies have been carried out for adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite [75], chemically modified plant wastes [76], industrial by-products such as lignin [77], diatomite [78], clino-pyrrhotite, lignite [79], aragonite shells [80], natural zeolites [81], clay [82], kaolinite and peat etc [83]. Another report showed zinc and copper removal from aqueous solutions using brine sediments, saw dust, and the mixture of both materials [84]. The potential to remove boron and arsenic from petrochemical wastewater by using aquatic booster was investigated in batch experiment process and the results were measured by inductively coupled plasma mass spectrometry (ICPMS). The main parameters influencing arsenic and boron adsorption onto the aquatic booster were contact time, size of particle, agitation speed, and dosage. The adsorption efficiency of arsenic and boron increases with longer contact time as well as more aquatic booster dosage and higher agitation speed. The removal efficiency for boron was around 60.36% by 35g/L dosage, 80 rpm and a particle size of 0.60 mm at of 390 minutes. As for the arsenic, the condition where it gives the removal percentage around 71.83% is that particle size of 0.6 mm, 300 minutes contact time, agitation speed of 80 rpm and dosage of 45g/L [85]. Hydrogels, which are cross linked hydrophilic polymers, a recapable of expanding their volumes due to their high swelling in water and hence are being used in purification of wastewater. Various hydrogels were synthesized and their adsorption behavior for heavy metals was investigated while Barakat and Sahiner (2008) prepared poly (3-acrylamidopropyl) trimethyl ammonium chloride hydrogels for As (V) removal [86].

Biosorption of heavy metals from aqueous solutions is a relatively new process that is effective and inexpensive and has been confirmed a very promising process in the removal of heavy metal from dilute waste waters such as oil field produced water. Typical biosorbents can be derived from three sources as follows: (1) non-living biomass such as bark, lignin, shrimp, krill, squid, crab shell, etc (2) algal biomass; (3)microbial biomass, e.g. bacteria, fungi and yeast. Different forms of inexpensive, non-living plant material such aspotato peels [87], sawdust [88], black gram husk [89], Rice husk [90-91], coffee husks [92], eggshell [93], seed shells [94], sugar-beet pectin gels [95].and citrus peels [96], sugarcane bagasse [97], coconut husk [98], oil palm shell [99], neem bark [100], fly ash have been widely investigated as potential biosorbents for heavy metals.

Algae, a renewable natural biomass proliferates ubiquitously and abundantly in the littoral zones of world has attracted the attention of many investigators as organisms to be tested and used as new adsorbents to adsorb metal ions. Several advantages in applying algae as biosorbent include the wide availability, low cost, high metal sorption capacity and reasonably regular quality Research works on the metal bio sorption using algal biomass include the biosorption of Cu_2 and Zn_2 using dried marine green macro alga Chaetomorphalinum [101], the biosorption of Cu_2, Cd_2, Pb_2 and Zn_2 using dried marine green macro alga Caulerpalentillifera [102], the biosorption of chromium from waste waterusing green alga Ulva lactuca [103], and the biosorption of lead (II) from wastewater by green algae Cladophorafascicularis [104]. Microbial removal of metal ions from wastewater has been indicated as being highly effective. Biosorption of heavy metals inaqueous solutions by bacteria includes Bacillus cereus [105], Escherichia coli [106], Pseudomonas aeruginosa [107]. Fungi and yeasts are easy to grow, produce high yields of biomass and at the same time can be manipulated genetically andmorphologically. Fungi biosorbents include *Aspergillus niger* [108], *Rhizopus arrhizus* [109], *Saccharomyces cerevisiae* [110] and *Lentinus edodes* [111].

Membrane filtration

Membrane filtration technologies with different types of membranes show great promise for heavy metal removal for their high efficiency, easy operation and space saving. The membrane processes used to remove metals from the wastewater are ultrafiltration, reverse osmosis, nano filtration and electrodialysis.

Ultrafiltration (UF) is a membrane technique working at low transmembrane pressures for the removal of dissolved and colloidal material. Since the pore sizes of UF membranes are larger than dissolved metal ions in the form of hydrated ions or as low molecular weight complexes, these ions would pass easily through UF membranes, hence to obtain high removal efficiency of metal ions, them icellar enhanced ultra filtration (MEUF) and polymer enhanced ultra filtration (PEUF) was proposed. MEUF was first introduced by Scamehorn et al. in the 1980s for the removal of dissolved organic compounds and multivalent metal ions from aqueous streams [112]. This separation technique is based on the addition of surfactants to wastewater in a quantity beyond its critical micelle concentration (CMC), the surfactant molecules will aggregate into micelles that can bind metal ions to form large metal-surfactant structures. The micelles containing metal ions can be retained by a UF membrane with pore sizes smaller than micelle sizes, whereas the un trapped species readily pass through the UF membrane. To obtain the highest retentions, surfactants of electric charge opposite to that of the ions to be removed must be used and metal removal efficiency by MEUF depends on the characteristics and concentrations of the metals and surfactants, solution pH, ionic strength, and parameters related to membrane operation. PEUF uses water-soluble polymer to complex metallic ions and forma macromolecular, having a higher molecular weight than the molecular weight cut off of the membrane which will be retained when they are pumped through UF membrane. The reverse osmosis (RO) process uses a semi-permeable membrane, allowing the fluid that is being purified to pass through it, while rejecting the contaminants and accounts for more than 20% of the world's desalination capacity [113]. Cu_2 and Ni_2 ions were successfully removed by the RO process and the rejection efficiency of the two ions increased up to 99.5% by using Na_2-EDTA [114]. The major drawback of RO is the high-power consumption due to the pumping pressures, and the restoration of the membranes. Nano filtration (NF) is the intermediate process between UF and RO and is a promising technology for the rejection of heavy metalions such as nickel [115], chromium [116], copper [117], and arsenic [118] from wastewater. NF process benefits from ease of operation, reliability and comparatively low energy consumption as well as high efficiency of pollutant removal; however reports have been published on use of NF and RO in combination for removal of copper from process waste water [119]. Electrodialysis (ED) is another membrane process for the separation of ions across charged membranes from one solution to another using an electric field as the driving force where ion-exchange membranes are used. This process has been widely used for the production f drinking and process water from brackish water and sea water, treatment of industrial effluents, recovery of useful materials from effluents and salt production [120].

Flotation Process

Flotation has nowadays found extensive use in waste water treatment and has been employed to separate heavy metals from a liquid phase using bubble attachment originated in mineral Processing. Dissolved air flotation (DAF), ion flotation and precipitation flotation are the main flotation processes for the removal of metal ions from solution. DAF is to allow micro-bubbles of air to attach to the suspended particles in the water, developing agglomerates with lower density than water, causing the flocs to rise through the water and accumulating at the surface where they can be removed as sludge [121]. Ion flotation method is based on imparting the ionic metal species in wastewaters hydrophobic by use of surfactants and subsequent removal of these hydrophobic species by air bubbles [122]. Potential of ion flotation was investigated to remove cadmium, lead and copper from dilute aqueous solution with a plant-derived biosurfactant tea sap on in [123]. Precipitate flotation process is another alternative of flotation method, based on the formation of precipitate and subsequent removal by attachment to air bubbles. Depending on the concentration of the metal solution, the precipitation may proceed by formation of metal hydroxide or as a salt with a specific anion (sulfide, carbonate, etc.) [124].

Electrochemical method

Electrochemical methods involve the plating-out of metal ions on a cathode surface and can recover metals in the elemental metal state; however these wastewater treatment technologies involve relatively large capital investment and the expensive electricity supply, so they haven't been widely applied. Electro coagulation (EC) involves the generation of coagulants *insitu* by dissolving electrically either aluminum or iron ions from aluminum or iron electrodes where, metal ion generation takes place at the anode, and hydrogen gas is released from the cathode that helps to float the flocculated particles out of the water [125]. This technique has been used with aluminium electrodes for removing Zn_2, Cu_2, Ni_2, Ag and Cr_2O_7 [126]. Electro flotation (EF) is a solid/liquid separation process that floats pollutants to the surface of a water body by tiny bubbles of hydrogen and oxygen gases generated from water electrolysis. EF has wide range applications in heavy metals removal from industrial wastewater and application of the optimized parameters on the separation of some heavy metal ions such as iron, nickel, copper, zinc, lead and cadmium was studied [127]. The Electro deposition has been usually applied for the recovery of metals from wastewater and is called a "clean" technology with no presence of the permanent residues for the separation of heavy metals [128].

Photocatalysis Process

In the recent years, photo catalytic process in aqueous suspension of semiconductor has received considerable attention in view of solar energy conversion and this photo catalytic process was achieved for rapid and efficient destruction of environmental pollutants. Upon illumination of semiconductor-electrolyte interface with light energy greater than the semiconductor band gap, electron-hole pairs (e-/h+) are formed in the conduction and the valence band of the semiconductor, respectively [129]. These charge carriers which migrate to the semiconductor surface, are capable of reducing or oxidizing species in solution having suitable redox potential. Various semiconductors have been used: TiO_2, ZnO,CeO_2, CdS, ZnS, etc. also a study showed photo catalytic degradation using UV-irradiated TiO_2 suspension for destroying complex cyanide with a con-current removal of copper [130].

Several studies were reported for the photo catalytic reduction of Cr (VI), which is mobile and highly toxic, compared to Cr (III), which is immobile and less harmful. Heterogeneous photo catalytic oxidation of arsenite toarsenate in aqueous TiO_2 suspensions has also been proved recently to be an effective and environmentally acceptable technique for the remediation of arsenite contaminated water. The process was performed using an adsorbent developed by loading iron oxide and TiO_2 on municipal solid waste meltedslag [131].

Biological methods

Various biological treatments, both aerobic and anaerobic can be used for heavy metal removal. A fixed activated sludge system (FAS) for treatment of wastewater containing heavy metal compounds (chromium, lead and nickel was carried out [132]. There results showed that a reduction of 84%, 75% and 80%, respectively was observed in chromium, lead and nickel on using fixed activated sludge at concentration of 1 mg/L. However, a reduction of 90%, 84% and 87%, respectively was observed by increasing concentration of them to 5 mg/L. Mechanism of activated sludge process was studied which showed that the carboxylic and amino groups are two main groups responsible for the binding properties of the biomass [133]. A novel bio filtration technique was utilized for the treatment of heavy metals mainly nickel, and their mechanism for heavy metals removal along with the kinetics of bio filters and its modeling aspects were studied [134]. The success in microbial cloning technique may improve the removal efficiency and hence the reduction in treatment cost. Trickling filter was used for removal of heavy metals, whereby the indigenous bacterial populations provided a certain advantage and ensured durability under various operating conditions. They operated the system in three different ways i.e. batch, continuous and sequencing batch reactor (SBR) with recirculation [135]. The use of an attached growth system provides the necessary surface for the development of bio film structures. Bio films provide high biomass concentration per unit volume, while bacteria can remain in the reactor for unlimited time, thus allowing the bacteria better adjustment to the environmental conditions. The studies on the metal removal from an aerobically digested sludge by chemical treatment and microbial leaching processes in laboratory reactors were carried out by addition of ferric sulphate that resulted into acidification of the sludge and elution of heavy metals from the sludge [136]. The investigation also showed that with an increase in the amount of iron added and decrease in the sludge concentration, the pH of the sludge decreased. They also observed that the Ferric iron eluted cadmium, copper and zinc effectively than sulphuric acid. This chemical method was found to be useful for the removal of heavy metals from aerobically digested sewage sludge. Attached growth waste stabilization ponds were used for heavy metal removal where experiments were conducted to investigate the performance of AGWSP units that received Cd and Cr shock loadings. Per the investigation, the waste stabilization pond (WSP) units without attached-growth media had more concentrations of the applied heavy metals present in the effluents than waste stabilization ponds [137].

Conclusions

Wastewater systems containing heavy metals with other organic pollutants, the presence of one species usually impedes the removal of the other. For instance, hydrometallurgy, a classical process to recover metals, is inhibited by the presence of organic compounds and a pre-treatment step, to remove or destroy organics, is generally required, pyro metallurgy which can decontaminate systems from organic pollutants and recover metals suffers from lack of controllability, demanding extremely high temperatures. The most promising methods to treat such complex systems are the photo catalytic ones which consume cheap photons from the UV-near visible region. These photo catalysts serve as electron relays, from the organic substrates to metal ions. Thus, they induce both degradation of organic pollutants and recovery of metals in one-pot systems, operable at traces of the target compounds(less than ppm). Although all above techniques can be employed for the treatment of heavy metal wastewater, it is important to mention that the selection of the most suitable treatment techniques depends on the initial metal concentration, the component of the wastewater, capital investment and operational cost, plant flexibility and reliability, environmental impact, utility of the treated water etc.

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