International Journal of Technical Innovation in Modern Engineering & Science (IJTIMES)
Impact Factor: 3.45 (SJIF-2015), e-ISSN: 2455-2585
Volume 4, Issue 4, April-2018

Removal of Heavy metal from wastewater using Nanofiltration; A Review

First Urmila K. Jadav[1]
Master of chemical Engineering,
G H Patel College of Engineering and Technology, V.V. Nagar, Gujarat, India
[1]Chemical Engineering Department, Gujarat Technological University, Email id: *jadavurmila@gmail.com*

Abstract— ***Industrial effluent containing heavy metals such as Arsenic, Cadmium, chromium, copper, Nickel, etc. produced from different industries such as electroplating, steel industries, and metal surface treatment processes. Effluents containing heavy metals may cause serious problem for human health and environment, because of their high solubility toxicity, non-biodegradability in the aquatic environments. There are various conventional techniques are available to remove heavy metal such as absorption, ion exchange, adsorption, coagulation, etc. these conventional techniques are consuming large amount of energy and time. Nowadays membrane separation processes like nanofiltration (NF) and ultrafiltration (UF) are used for removal of heavy metal because their high flexibility, energy saving and simple in construction. Concentration Polarization and membrane fouling are the key initiators to decline the permeate flux in a membrane separation processes. Among all these conventional technique membrane separation process is technically easy to separate heavy metals from wastewater. The Nanofiltration have lower operating pressure and high flow rates, Nanofiltration inexpensive than Reverse Osmosis. Present study discussed for Nanofiltration combine with surfactant and various parameters like pressure, concentration, pH, and cross flow velocity on chromium rejection and permeate flux of the membrane.***

Keywords— Heavy metals, Nanofiltration, Surfactant, Rejection and Flux decline.

I. INTRODUCTION

Large quantities of water and water steam are used for cooling, heating and washing purposes, in industry as well as domestically use. Water is an excellent solvent for a wide variety of chemical substances; such as it is widely used in industrial processes. Large amount of waste water is generated in the industry, it is necessary to reuse and as it give impact on eco system. We can recycle water by removing impurities such as COD, BOD, total dissolved solid, total suspension solid, organic and inorganic contaminants from waste water upto acceptable amount. It can reused in several ways and give many benefits in industry, reuse of water has potential to reduce the cost of water, increase its availability, improve community relations, increased productivity per unit water amount, lower the waste water discharge and their pollutant load and reduce the thermal energy. Therefore, necessary for large amount of water in our daily requirement waste water treatment is important goal. It was studied that one of the major serious problems of heavy metal in such waste water which are produced many way. With the rapid development of industries such as metal plating facilities, metal coating, smelting and refining of non-ferrous metals and mineral processing and metallurgical operations, etc., heavy metals are directly or indirectly discharged into the aquatic environment. The heavy metals like Pb, Cd, Zn, Cu, Ni, Hg, Cr etc. present in the waste water is persistent and non-degradable in nature. Moreover, they are soluble in aquatic environment and thus can be easily absorbed by living cells, microorganisms and thus entering in food chain (Fenglian et. al, 2010). Therefore, treatment of heavy metals containing industrial effluent becomes quite important before being discharged into the environment. The environmental engineers and scientists are therefore facing a tough task for cost effective treatment of waste water containing heavy metals. The conventional methods for heavy metal removal from waste water includes chemical precipitation, chemical oxidation, ion exchange, Absorption and Adsorption, electro dialysis, etc. These methods are not very effective, they are costly and require high energy input and more time consuming.

These methods are associated with formation of toxic sludge, disposal of which renders it expensive and non-eco-friendly in nature. Nowadays, number of approaches has been investigated for safe and economical treatment of heavy metal laden waste water (Tripathi A. et. al., 2015). Membrane filtration has received remarkable attention for the treatment of heavy metal containing effluent. It is capable of removing suspended solid, organic compounds and inorganic contaminants. Depending on the size of the particle that can be retained, various types of membrane filtration such as Ultrafiltration, Nanofiltration and Reverse Osmosis can be employed for heavy metal removal from waste water (Gunatilake S. K., 2015).

In this review, process involved a combination of surfactant and Nanofiltration process for the separation of heavy metal ions. The surfactant forms roughly spherical aggregates which called micelles it contain about 50 to 100 molecules, it can trap metal ions, this aggregates are retained and only water permeate flux is passed though the membrane (Morel G. et al, 1990). This review paper various factors affect such as initial concentration of feed and surfactant, operating pressure, crossflow velocity and pH etc. on the permeate flux and Chromium rejection.

II. LITERATURE REVIEW

2. Heavy metal

Heavy metals are natural compounds which occurs from the earth's crust. Heavy metal refers to any metallic chemical essence that has a relatively high densities, high atomic weight and atomic numbers and also high toxic and poisonous at low concentrations (Singh M. et.al. 2016). Heavy Metals are basically considered those whose density exceeds 5 g per cubic centimetre (Barakat, 2010; Gunatilake S.K., 2015). There are around 20 metals which are fall down into this category such as lead (Pb), cadmium (Cd), chromium (Cr), zinc (Zn), nickel (Ni), mercury (Hg), Copper (Cu) etc. These heavy metals are cannot destroyed and degraded. They are highly soluble in water and are given chronic effect on aquatic environment and human health. Heavy metals used in industrial, domestic, agricultural, medical and technological application an as result they are discard at wide range in our environment.

2.1 Heavy metal sources

Heavy metals are produced and released from various chemical industries. Electroplating and metal surface treatment processes produces significant quantities of waste waters which is containing heavy metals; such as cadmium, zinc, lead, chromium, nickel, copper, vanadium, platinum, silver, and titanium from a variety of applications (Tripathi A.et.al.,2015). Apart from this waste water also generated from leather tannery, textile, pigment & dyes, paint, wood processing, petroleum refining industries and photographic film production contains significant amount of heavy metals. These heavy metal ions are toxic for both human beings and animals and living microorganisms. Other main source of heavy metals from printed circuit board manufacturing and tin, lead, and nickel solder plates are the most widely used resistant over plates (Gunatilake S.K.,2015). Another sources for the metal wastes include; the wood processing industry where a chromated copper-arsenate wood treatment produces arsenic containing heavy metals; inorganic pigment manufacturing producing pigments that contain chromium compounds and cadmium sulfide; petroleum refining which generates conversion catalysts contaminated with nickel, vanadium, and chromium; and also photographic operations producing high concentrations of silver and Ferro cyanide (Barakat M. A., 2010; Gunatilake S.K.,2015).

2.2 Heavy metal toxicity

Heavy metals are very toxic and carcinogenic, they are highly soluble in water and it can absorbed by living microorganisms and accumulated in human body. They cause serious health problems such as reduced growth and development, stunted growth, damage to vital organs, damage to brain, cancer and in some cases death also. Waste water regulations were established to minimize human and environmental disinterment to hazardous chemicals. These include limits on the types and concentration of heavy metals that may be present in the discharged waste water (Gunatilake S.K., 2015; Tripathi A. et. al., 2015; Barakat, 2010). The maximum contaminant level (MCL) standards, for those heavy metals established by United State Environmental Protection Agency (USEPA) (Abbasi E. et.al. 2012; Gunatilake, 2015; Tripathi A. et. al., 2015). The Maximum Contaminant level (MCL) and Different metals effect on health summarized in below table.

Table -1: The MCL standards for the most hazardous Heavy metals and their toxicities (Babel et. al., 2003; Gunatilake S.K., 2015; Barakat M.A., 2010).

Heavy Metals	Toxicities	MCL (mg/L)
Arsenic	Skin manifestations, visceral, cancer, vascular disease.	0.05
Cadmium	Kidney damage, renal disorder, Human carcinogen	0.01
Chromium	Headache, diarrhea, nausea, vomiting, Carcinogenic	0.05
Copper	Liver damage, Wilson disease, insomnia	0.25
Nickel	Dermatitis, nausea, chronic asthma, coughing, Human carcinogen	0.20
Zinc	Depression, lethargy, neurological signs and nervous system	0.80
Lead	Damage the fetal brain, diseases of the kidneys, circulatory system and nervous system	0.006
Mercury	Rheumatoid arthritis, and diseases of the kidneys, circulatory system and nervous system.	0.00003

2.3 Need for the removal of heavy metals

It was studied that continuous discharge of industrial, domestic and agricultural wastes in rivers and Lakes causes deposit of pollutants in sediments. Such pollutants include heavy metals, which Imperil public health after being incorporated in food chain. Heavy metals cannot be destroyed through biological degradation, as is the case with most organic Pollutants. Incidence of heavy metal accumulation in fish, oysters, mussels, sediments and other components of aquatic ecosystems have been reported from all over the World. Excessive amounts of some heavy metals can be toxic through direct action of the metal or through their inorganic salts or via organic compounds from which the metal can become easily detached or introduced into the cell. Exposure to different metals may occur in common circumstances, particularly in industrial setting. Accidents in some environments can result in acute, high level exposure. Some of the heavy metals are toxic to aquatic organisms even at low concentration.

3. Conventional processes for heavy metal removal

Heavy metal removal from waste water can be achieved by conventional treatment processes such as chemical precipitation, Coagulation and Flocculation, Ion Exchange, Electrochemical treatments, Physico- Chemical Treatment, Biosorption, activated carbon adsorption, etc. (Zargar F.H.,2012; Gunatilake S.K, 2015; Dhokpande S.R., 2013).

There are different technique used for heavy metal removal, which summarised below:

3.1 Chemical precipitation

Chemical Precipitation Process is one of the most widely used for heavy metal removal from contaminant waste water in industry because of simple operation and this chemical precipitation processes produce insoluble metal precipitation by reacting dissolved metals in the solution and precipitant (Gunatilake S. K., 2015). Chemical Precipitation processes involve the addition of chemical reagents such as alum, lime, iron salts and other organic polymers (Lakherwal D, 2014; Ahalya N. et. al., 2003). Chemical precipitation is very easy and cheapest process. No high installation charges, but it has some disadvantages like sludge formation and its disposal problems.

The conceptual mechanism of heavy metal removal by chemical precipitation is presented equation (1) (Barakat, 2010):

$$M^{2+} + 2(OH)^{-} \longleftrightarrow M(OH)_2 \downarrow \qquad \text{eq.(1)}$$

Where M^{2+} and $(OH)^{-}$ represent the dissolved metal ions and the precipitant, respectively, in which $M(OH)_2$ is the insoluble metal hydroxide (Barakat M. A., 2010). Once the metals precipitate and form solids, they can easily be removed, and low metal concentration can be discharged. The most commonly used precipitation technique is hydroxide treatment due to its simplicity, low cost of precipitant such as lime, and ease of automatic pH control (Gunatilake S. K., 2015). pH adjustment to the condition is major parameter that significantly improves chromium removal by chemical precipitation. The disadvantage include high amount of chemicals to reduce metals to an acceptable level for discharge. Other drawback is the large amount of sludge production that requires further treatments and slow metal precipitation, poor settling and the long- term environmental impacts of sludge disposal (Barakat M.A., 2010).

3.2 Coagulation and flocculation

Coagulation is a most common one process out of the different conventional processes that occurs when coagulant is added to water to “destabilize” colloidal suspensions. Conversely, flocculation process involves the addition of polymers that clump the small, destabilized particles together into larger aggregates so that they can be more easily separated from the water. Coagulation is a chemical process that involves neutralization of charge whereas flocculation is a physical process and dose not involves neutralization of charge. Coagulation and flocculation are an essential part of drinking water treatment as well waste water treatment. Coagulation is the chemical reaction which occurs by the addition of chemical or coagulant to the water. The basically coagulant substance is alum is generally used in coagulation process. The coagulant encourage the colloidal material in the water to join together into small aggregates called “flocs”. Suspended matter is then attracted to these flocs. Flocculation is a slow gentle mixing of the water to encourage the flocs to form and grow to a size which will easily settle out (Lakherwal D., 2014).

3.3 Ion exchange process

Ion-Exchange processes is used successfully in the industry for the removal of heavy metals from waste water. Ion-Exchanger is a solid capable of exchanging either cations or anions from the surrounding materials. Ion exchange resin, are synthetic organic or natural solid resins (Barakat M.A, 2010; Fenglian et.al. 2010). Ion exchange resins are water-insoluble solid substances which can absorb positively or negatively charged ions from an electrolyte solution, the positively charged ions in cationic resins such as hydrogen and sodium ions are exchanged with positively charged ions, such as nickel, copper and zinc ions, in the solutions. Similarly, the negative ions in the resins such as hydroxyl and chloride ions can be replaced by the negatively charged ions such as chromate, sulfate, and nitrate and dissolved organic carbon (DOC). The most common cation exchangers are strongly acidic resins with sulfonic acid groups ($-SO_3H$) and weakly acid resins with carboxylic acid groups (-COOH). Hydrogen ions in the sulfonic group or carboxylic group of the resin can serve as exchangeable ions with metal cations. As the solution containing heavy metal passes through the cations column, metal ions are exchanged for the hydrogen ions on the resin with the following ion-exchange process (Fenglian et.al. 2010):

$$nR\text{-}SO_3H + M^{n+} \longrightarrow (R\text{-}SO_3^{-})_nM^{n} + nH^{+} \qquad \text{eq. (2)}$$

$$nR\text{-}COOH + M^{n+} \longrightarrow (R\text{-}COO^{-})_nM^{n+} + nH^{+} \qquad \text{eq. (3)}$$

The Disadvantages of this ion exchange process includes; High cost and partial removal of certain ions (Ahalya N. et. al. 2003). Another drawbacks of this process is, it cannot handle concentrated metal solution as the matrix gets easily fouled by organics and other solids in the waste water. Moreover ion exchange is non selective and other solids in the waste water (Barakat M.A., 2010).

3.4 Electro chemical treatment

Electrolytic recovery or electro-winning is one of the many technologies used to remove metals from Industrial waste water streams. This process uses electricity to pass a current through an aqueous metal-bearing solution containing a cathode plate and an insoluble anode (Barakat M.A., 2010). Electricity can be generated by movements of electrons from one element to another. Electrochemical process to treat waste water containing heavy metals is to precipitate the heavy metals in a weak acidic or neutralized catholyte as hydroxides. Electrochemical treatments of waste water involve electro-deposition, electro-coagulation, electro-flotation and electro-oxidation (Gunatilake S.K., 2015). A noticeable disadvantage was that corrosion could become a significant limiting factor, where electrodes would frequently have to be replaced (Barakat M.A., 2010).

3.5 Biosorption

Biosorption is another relatively new process that has been used to remove heavy metals from waste water (Fenglian et.al. 2010). Sorption process is transfer of ions from solution phase to the solid phase, actually describes a group of processes, which includes adsorption and precipitation reactions. Adsorption has become one of the alternative treatment techniques for waste water. Basically, adsorption is a mass transfer process and substances bound by physical and or chemical interactions to solid surface (Gunatilake S.K., 2015).

The major advantages of Biosorption are its high effectiveness in reducing the heavy metal ions and the use of inexpensive biosorbents. Biosorption processes are particularly suitable to treat dilute heavy metal waste 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.

3.6 Physico- chemical treatment:

Physical separation consists of mechanical screening, hydrodynamic classification, gravity concentration, flotation, magnetic separation, electrostatic separation, and attrition scrubbing. Physical separation techniques are primarily applicable to particulate forms of metals, discrete particles or metal-bearing particles. The efficiency of physical separation depends on various soil characteristics such as particle size distribution, particulate shape, clay content, moisture content, humic content, heterogeneity of soil matrix, density between soil matrix and metal contaminants, magnetic properties, and hydrophobic properties of particle surface (Gunatilake S.K., 2015).

3.7 Activated carbon adsorption:

Activated carbon adsorbents are widely used in the removal of heavy metal contaminants. Its usefulness derives mainly from its large micropore and mesopore volumes and the resulting high surface area. A large number of researchers are studying the use of activated carbon for removing heavy metals. To make progress in heavy metals adsorption to AC without the expense of decline in the pollutants adsorption, additives and AC composite could be an option (Fenglian Fu. et. al., 2010). Activated carbon is the most widely used adsorbent. It is a highly porous, amorphous solid consisting of micro crystallites with a graphite lattice, usually prepared in small pellets or a powder. It can remove a wide variety of toxic metals (Lakherwal D., 2014). Adsorption process being very simple, economical, effective and versatile has become the most preferred methods for removal of toxic contaminants from waste water. This paper reviews the use of various readily available natural materials as adsorbents of heavy metals from industrial waste water. Various low cost adsorbents reviewed includes sand, waste tea leaves eggshell, rice husk, activated carbon, zeolites, olive stones, wood sawdust etc. (Lakherwal D., 2014). Many researcher work with agriculture waste used as adsorbent. Some cases for requiring high percentage of heavy metal removal adsorbent with modification surface is study in recent work.

Nowadays adsorbent is used with new modification surface and developing low cost, biological, biosorption adsorbent is important role for heavy metal removal.

Table-2: The advantages and disadvantages of the various Physico-chemical method for treatment of heavy metal removal; (Barakat M.A., 2010)

Sr. No.	Treatment Method	Advantages	Disadvantages
1	Chemical Precipitation	Low capital cost, simple operation.	Sludge generation, extra operational cost for sludge disposal.
2	Coagulation/ Flocculation	Simple operation, low capital cost	Production of sludge, transfer of solid compound in solid phase.
3	Ion Exchange Processes	Removal of metals and organic and inorganic ions	High cost and partial removal of certain ions, Easily Fouled.
4	Photocatalysis	Removal of metals and organic pollutant simultaneously, less harmful by-products	Long duration time, limited applications.
5	Adsorption with Common Adsorbent	Low Cost Operation, Removal of Metals	Produce Biological Waste

3.8 Nanofiltration Process:

NF process is a pressure driven process. In this membrane separation process 'membrane' act as selective barrier which restrict the passage of pollutants such as organic, nutrients, turbidity, microorganisms, inorganic metals ions etc. and passes the clear water through it (Shon H.K. et al., 2013). Several studies have been done on the application of NF. Many researchers work on NF separation process because of its simple design, high efficiency, low floor space (Fenglian Fu et al., 2010) and increasing the water quality and reuse in industries.

NF provides the higher retention than UF and lower operating cost than RO. Due to the lower operating pressure (1-10 bar) and higher flow rates, NF is inexpensive when compared to other membrane processes. NF is the novel technology than RO that generally used to separate relatively small organic and inorganic compounds (Zargar F. H., 2012). NF membranes allow partial permeation of monovalent salts while rejecting bivalent salts and hardness to a greater extent from aqueous solutions. NF can reduce lower TDS and hardness, color and odor, and remove heavy metal ions from ground water (Abhang R.M. et al., 2013). Other possible applications covered treatment of effluents from textile dyeing, bulk drug, chemical process industries and pulp-bleaching also fermentation broths, demineralization in dairy industry (Shon H.K. et. al., 2013). The most notable difference is the ability of NF membranes to selectively reject bivalent ions, while passing monovalent ions. It is a common belief that NF and RO membranes do not have distinct pores, as in ultrafiltration and Microfiltration membranes. The mechanism of transport and rejection of NF membrane is quite complex and is still a point of debate between scientists.

4. Conclusion

A review of various conventional processes and nanofiltration technique for removal of heavy metals from wastewater shows that nanofiltration process has great potential to remove heavy metals. Many researchers work on this heavy metals removal from industrial wastewater using nanofiltration. More studies should be carried out for efficiently high amount of heavy metal removal at low cost with easy operation by using nanofiltration process.

References

- Abhanga R. M., Wanib K.S., Patilc V.S., Pangarkara B.L., Parjanea S.B., "Nanofiltration for Recovery of Heavy Metal Ions from Waste Water - A Review", (2013), Int. J. of Res. in Envi. Sci. and Tech., 2249–9695.
- Ahalya N., Ramachandra T.V., and Kanamadi R. D. "Biosorption of Heavy Metals", (2003), Res. J. of Chem. and Envi. 7, 4.
- Baek K., Yang J. W., (2004) "Micellar- Enhanced ultrafiltration of chromate and nitrate: binding competition between chromate and nitrate", J. of Desalination, 111-118.

- Bhat M. A., Mukhtar F., Chisti H., Shah S. A., "Removal of heavy metal ions from Waste water by using oxalic acid: an Alternative method", (2014), Int. J. of Latest Res. in Sci. and Tech., 3, 61-64.
- Barakat M.A., "New trends in removing heavy metals from industrial waste water", (2011), Arabian J. of Chem., 4, 361–377.
- Daniş U, Keskinler B., "Chromate removal from waste water using micellar enhanced crossflow filtration: effect of transmembrane pressure and crossflow velocity", (2006), J. Int. Envi. Appli. & Sci., 3-4, 91-97.
- Fenglian F., Wang Q., "Removal of heavy metal ions from waste waters: A review", (2010), J. of Envi. Manag. 97,407-418.
- Gunatilake S.K., "Methods of Removing Heavy Metals from Industrial Waste water", (2015) J. of Mult. Engi. Sci. Stud. (JMESS), 1, 2912-1309.
- Garravand E. A., "Removal of Cr (VI) and Cr (III) From Water by Reduction and Micellar Enhanced Ultrafiltration Techniques", A Thesis, (2012) Concordia University Montreal, Quebec, Canada.
- Hosseini S. S., Nazif A, Shahmirzadi M. A. A., Ortiz A, (2017) "Fabrication, tuning and optimization of poly (acrilonitryle) nanofiltration membranes for effective nickel and chromium removal from electroplating waste water", J. of Sep. and Puri. Tech., 187, 46–59.
- Illias S., (2002) "Flux enhancement in crossflow membrane filtration: Fouling and It's minimization by flow reversal".
- Jaber S, "Removal of Heavy Metals Pb2+, Cu2+, Zn2+, Cd2+, Ni2+, Co2+ and Fe3+ from Aqueous Solutions by using Xanthium Pensylvanicum", (2013), Leonardo J. of Sci., 97-104.
- Lakherwal D., "Adsorption of Heavy Metals: A Review", (2014), Int. J. of Envi. Res. and Dev., 4, 41-48.
- Mikulasek P., Cuhorka J., "Removal of Heavy Metal Ions from Aqueous Solutions by Nanofiltration", (2016), A publ. of the Italian Asso. of Chem. Engi., 47.
- Morel G., Graccia A., Lachaise J., (1991) "Enhanced nitrate ultrafiltration by cationic surfactant", J. of Memb. Sci., 1-12.
- Niaki SM D., Takdastan A., Bazafkan M.H., and Zazouli M.H., "Survey of Nanofiltration Technology In Removing Heavy Metals (Ni, Cu and Zn) From Industrial Waste Water", (2015), Int. Conf. on Chem. Envi. and Bio. Sci. 18-19.
- Nath K., Patel T. M., Dave H. K., (2015) " Performance characteristics of surfactant treated commercial polyamide membrane in the nanofiltration of model solution of reactive yellow 160", J. of Water Pro. Engi. 111.
- Nath K., "Membrane separation process", PHI learning pvt ltd, new delhi, 8 (2011) 89-98.
- Poźniak G, Poźniak R, "Modified polyethersulfone membranes for micellar enhanced ultrafiltration of chromium", (2007), Pro. of European Con. of Chem. Engi., 16-20
- Raouf MS A., Raheim ARM A., "Removal of Heavy Metals from Industrial Waste Water by Biomass-Based Materials: A Review", (2017), J. of Pollu. Effe. & Cont. 5:1.
- Racho P., Phalathip P., "Modified Starch–Enhanced Ultrafiltration for Chromium (VI) Removal", (2014) J. of Clean Ener. Tech., 2.
- Shon H. K., Phuntsho1 S., Chaudhary D. S., Vigneswaran S., and J. Cho, "Nanofiltration for water and waste water treatment –a mini review", (2013), published in Drink. Water Eng. Sci.
- S. R., Kaware J. P., "Biological Methods for Heavy Metal Removal- A Review", (2013), Int. J. of Engi. Sci. and Inv. Tech. (IJESIT).2.
- Singh M., Varghese S., (2016), "Conventional and innovative techniques for removal of heavy metals from electroplating industry waste water", Int. J. of Eng. Sci. & Res. Tech., 3,150-159.
- Tripathi A. et. al., 2015, "Heavy Metal Removal from Waste water Using Low Cost Adsorbents", (2015), J. of Biore. and Biodeg. 6:6.
- Wenten I. G., "Ultrafiltration in water treatment and its evaluation as pre-treatment for reverse osmosis system".
- Zargar F. H., "Separation of Hexavalent Chromium from Water Using Nanofiltration", (2012), Int. Conf. on Tra. Tour. and Manag, (ICTTM) 21-22.