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# **CHAPTER 1**



## **INTRODUCTION**

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## **1. Introduction**

### **1.1 Water pollution**

Water is essential for life and plays very important role in maintenance of global flora and fauna. Many countries are facing the acute problem of water pollution today. The fresh water bodies are highly contaminated due to anthropogenic activity globally. The polluted water has adverse effect and is real challenge to survival.

The nature of pollutants varies according to the source of water pollution. These pollutants are introduced into natural water by untreated industrial effluents, municipal sewage, pesticides from agricultural fields and pharmaceuticals etc (Ali et al., 2012, Chowdhury et al., 2011, Ponnusami et al., 2007). There are other sources of water pollutants such as run-off from mining field, septic tank and penetration of solid waste into ground water.

### **1.2 Types of water pollutants**

The water pollutants are classified according to nature and occurrence. These pollutants may be present in the form of organic, inorganic and radioactive materials and thermal pollutants. The organic and inorganic pollutants are responsible for higher level of pollution in water bodies.

#### **1.2.1 Organic Pollutants**

The dyes and pesticides are the main source of organic pollutants (Trivedi et al., 2016). The other organic pollutants are detergents, pathogens, sewage, other synthetic organic compounds and oxygen demanding wastes.

#### **1.2.2 Inorganic Pollutants**

The different types of pollutants such as metallic compounds, inorganic salts, and mineral acid mine drainage and trace metals are included in the category of inorganic

pollutants. The other chemicals such as chlorides, nitrates, sulphates, bicarbonates and hydrogen sulphides etc. may also be included in the group of inorganic pollutants.

### **1.2.3 Sediments**

The sediments are introduced into water bodies by natural processes. The most of rivers are polluted by these sediments. These sediments are comprise organic and inorganic substances which decompose and affect the water bodies by leaching out, the undesired material into the fresh water. The amount of suspended particle is much higher than the solid content of sewage. These sediments also contain the heavy metals such as Cu, Ni, and Cr. Some of These heavy metals become carcinogenic and harmful to the aquatic animals and humans after leaching out.

### **1.2.3 Radioactive materials**

In this group, the radioactive elements like as uranium and thorium are included. The gaseous waste from fuel element and the radioactive fission products are also included in this category.

### **1.2.4 Thermal pollutants**

Water is used as common coolant in most industries which raises the temperature of natural water. The increased temperature of water decreases the dissolved oxygen into the water and this water is not suitable for respiration of aquatic animal like fish. Hot water discharge in lakes and streams also affects the chemical cycle causing change in chemical equilibrium in the water mass.

## **1.3 Pollution by heavy metals**

The heavy metals are the elements with atomic weight between 63.5 and 200.6 with specific gravity more than 5.0 (Srivastava et al., 2008). These heavy metals are

inorganic in nature and most have carcinogenic effect at very low concentrations. The heavy metals are non biodegradable in nature which leads to unbalance in the food chain. These metals cause bad health effects such as damage of liver, kidneys and lungs, reduced growth and development of organs, and unusual behaviour of mental and nervous systems (Zhang et al., 2016; Koedrith et al., 2013). Long term presence of these heavy metals may cause various types of cancers, Alzheimer and Parkinson disease. The presence of these metals also affects the metabolic pathway of living organisms by interruption of the carboxylic bond, affecting amino acid group and sulphur bonds present inside the cell of humans and animals (Qu et al., 2013). The high concentrations of these metals cause death of animal through carcinogenic and mutagenic effects, and lead to long term accumulation of these metals into living cell.

The heavy metals are introduced into water bodies by natural as well as human interruption. The natural sources of heavy metal include the drainage of ore containing rocks which contains many metals. The anthropogenic source of heavy metals comprise of untreated wastewater containing metal bearing effluents of industrial area, mining operations, agricultural drainage of fertilizers and atmospheric deposition of vehicular emission (Fu and Wang, 2011; Clemens and Ma, 2016). The effluents of various industries such as metal plating, tanneries, fertilizer, paper etc are hazardous for living being (Raval et al., 2016). Other sources of toxic heavy metals are wood processing industry containing arsenic metal; petroleum industries which contains nickel, vanadium and chromium metal catalysis; pigment and paint industries which contain lead, cadmium and chromium compounds; leather tanneries which contains chromium; manufacturing industry of tin, lead, and nickel ( Han et al., 2016 ). Due to high toxicity of these hazardous heavy metals, the effluents of industries are considered seriously and before discharge into running water bodies, the treatment of this waste

water is needed. The toxic metals which are of great concern include arsenic, zinc, copper, nickel, mercury, cadmium, lead and chromium which is must be treated before discharge into environment (Dhir et al., 2009). For this many industrialized countries have sticter waste water regulations and concentration limit of these metals bearing waste water before discharge.

### **1.3.1 Pollution by Cr (VI) metal**

Chromium is present in industrial effluents produced from electroplating, leather tanning, cement, mining, textile dyeing, dye manufacturing, paper, ink, aluminium conversion coating operations, steel fabrication, plants producing industrial inorganic chemicals, wood treatment units, paints and pigments, metal cleaning, fertilizer and photography industries and cause severe environmental and public health problems (Anupam et al., 2011; Tan et al., 2015). In general, industrial wastes contain both hexavalent and trivalent forms of chromium (Nakajima et al., 2004). The Cr (III) is nearly insoluble and hence aqueous concentrations are usually well below the water quality standards (Anderson et al., 1994). The hexavalent species are relatively more soluble and are 500 times more toxic than the trivalent species (Gupta et al., 2009). It is proven to cause skin irritation, epigastric pain, nausea, vomiting, severe diarrhea, hemorrhage and carcinogenicity in humans (Mohanty et al., 2005; Wang et al., 2014). The high level of chromium concentration is expected in the wastewater emanating from chrome recovery unit of leather units using chrome tanning. According to the World Health Organization (WHO), the permissible level in surface water bodies for Cr (VI) should be lower than 0.05 mg/L. Therefore, it is necessary to reduce Cr (VI) to acceptable levels before discharging of effluents into aquatic environments.

## 1.4 Pollution by dye solution

Dyes are categorized as important class of water pollutants which are introduced into the aqueous phase by the effluent of textile and dye manufacturing industries (Dawood et al., 2014). Dyes affect the water bodies because these are highly soluble in water and non- biodegradable in nature (Crini, 2006). The high concentration of dyes reduces the sunlight penetration into water bodies which affect the photo synthesis process of aquatic weeds (Bouguettoucha et al., 2016). The dye solution also changes other characteristics of water like pH, BOD and COD (Dardouri and Sghaier, 2017).

The chemical structures of dye are consisting of aromatic compounds and some heavy metals due to which these dyes are toxic and of great concern to aquatic and human health (Imran et al., 2015). The skin irritation is also occurs due to contact of dye effluent with human skin. After evaporation of hazardous chemical present in dye effluent may also affect the eye sight and permanent eye injury. It can also cause bad effect on human organs such as damage of liver and kidney; reproductive system of animal and damage of central nervous system (Tan et al., 2008).

Dyes are used for colouring the raw materials or final products of industries such as textile, leather, paper, food processing, plastics, rubber, printing, carpet and dye manufacturing industries (Zhou et al., 2019; Ravi et al., 2005; Hashem et al., 2007). There are nearly 10,000 different dyes and pigments which are being used in many industries to colour the products (Ogugbue and Sawidis, 2011). In comparison to many dye utilizing industries, the textile industry produces highest amount of dye stuff material. The textile industry produces 10,000 tonnes dye material per year worldwide (Katheresan et al., 2018). Due to toxic effect of dye, the waste water containing these dye stuff must be treated before discharge into water bodies.

### **1.4.1 Pollution by methylene blue Dye solution**

The nature of methylene blue (MB) dye is cationic and it is utilized in medical for staining and for colouring material in textile industries which produces dark coloured polluted water. This polluted water causes low penetration of sunlight due to coverage of receiving water and it harms the health of flora and fauna (Kumar et al., 2011; Tan et al., 2007). Therefore before discharge of this polluted water, it is a need to remediate for healthy environment.

## **1.5 Waste water treatment techniques**

Different techniques have been employed for treatment of metal and dye bearing waste water. The most common technique which are being used for treatment of metal and dye containing waste water are chemical precipitation, electro-dialysis, ion-exchange and adsorption etc.

### **1.5.1 Precipitation method**

This method is the oldest method and generally used as a conventional technique for the removal of metal from waste water (Tanong et al., 2017). For this purpose, many chemical reagents such as caustic soda, soda ash and sodium sulphide are used as the precipitating agents. The addition of these chemicals changes the pH of solution and the precipitation of metal occurs (Hashim et al., 2011). This process is ineffective at lower concentration of metal and hence the incomplete removals of metal is a problem. This process produces a large amount of sludge with high amount of water content due to precipitates of metals. The sludge disposal is a problematic. For the removal of precipitates, filtration and sedimentation are also required an additional processes. For the removal of precipitates, additional methods like filtration and sedimentation processes are also required which add to cost of treatment.

### **1.5.2 Reverse osmosis**

This is a filtration process which is operated by pressure. The pressure is used as a driving force to charge the untreated solution into semi-permeable membrane (Bilal et al., 2013). In this process, large volume of brine disposal is the main problem. The high operational cost and membrane fouling are also the limitations of this process. For this process, the pre-treatment of waste water is also required to get desired productivity of water (Hosseini et al., 2016). For pre-treatment, ultrafiltration process is used for removal of membrane clogging problem. It also changes the property of water such as pH, temperature and chemical constituents.

### **1.5.3 Ion- exchange**

Ion-exchange is a separation process used for the removal of ionic constituents from waste by ion exchange resin (An et al., 2011). The saturated resin became further reusable by treatment with acid or basic solutions, and this regeneration process, generates the secondary pollutant. The ion-exchange resin is also affected by complex forming material of effluent which also reduces the efficiency of removal. The initial cost of for installation is also high and it is not economical for waste water treatment.

### **1.5.4 Electrodialysis**

In electrodialysis method, an ionic membrane is used to transfer the ions by applying the electricity across the membrane which allows the transfer of anions and cations through membrane (Coman et al., 2013). In this process of effluent treatment, the use of chemicals is very low, with high recovery of treated water. The problem of membrane clogging with scaling is also encountered during effluent treatment.



## 1.6 Adsorption

The adsorption is used as an efficient and preferable method for the removal of heavy metals and dyes from waste water solution (Vunain et al., 2016). The quality of treated effluent is good in comparison to that obtained with other waste water treatment methods. In this treatment method, the molecules of waste material are trapped on the active surface of adsorbent by mass transfer operation. In the process of adsorption, accumulation of adsorbate molecule on the surface of adsorbent occurs by interaction of two phases. The substance on which adsorption process occurs is called adsorbent and the molecules being accumulated on the surface of adsorbent are termed as adsorbate. In comparison to other conventional methods, the adsorption process is preferred problem for the removal of heavy metal and dye from aqueous solution due to low cost of operation and less fouling (Sharma et al., 2017). The use of adsorption process is easy and flexible which has a simple design for easy operation. In this process, the production of secondary pollutants is very less, and the adsorbent material can also be regenerated which makes it as environmentally acceptable method (Demirbas, 2008). Many researches have carried out for the development of adsorbent material with high surface area (Ewecharoen et al., 2009). For selection of adsorbent, it is required that the raw material should have low cost, easily available and abundant in quantity. The other property such as porous structure, functional group of adsorbent also helps in the selection of good adsorbent.

### 1.6.1 Type of adsorption

The interaction of adsorbent and adsorbate molecules is governed by different force. On the basis of these forces adsorption is classified as physical and chemical adsorption.

### **1.6.1.1 Physical adsorption**

In physical adsorption, the interaction between adsorbate molecules with the adsorbent is governed by physical forces such as van-der Waal's force and hydrogen bond etc. In this adsorption process the adsorbed molecules do not stick to a particular site on the adsorbent surface, but are free to translational displacement over interface of adsorbent. At the preferable condition of temperature and pressure, the adsorbed molecules can accumulate at one position and make a multilayer having thickness of several diameters. The heat of adsorption is in the order of  $42 \text{ KJmol}^{-1}$  ( $5-10 \text{ kcal mol}^{-1}$ ). Usually the process of physical adsorption is fast, and reversible at aseptical condition of concentration and temperature.

### **1.6.1.2 Chemisorption**

In chemisorptions, the attachment of adsorbate molecules on the surface of adsorbents is occurs due to chemical bond between them. The force of attraction is stronger in chemical adsorption which is comparable with bond of chemical compound. In chemical adsorption, the attraction of molecules may be exothermic or endothermic in nature, and the temperature affects the extent of adsorption. The adsorbate molecules form the monolayer on the surface of adsorbent and no translational motion is made by the adsorbed molecules. For this adsorption process, the heat of adsorption is found to be more than  $83 \text{ kJ mol}^{-1}$  ( $15-30 \text{ kcal mol}^{-1}$ ) and the attachment of molecules are generally irreversible.

### **1.6.2 Adsorption from solution**

In adsorption, adsorbate molecule has a tendency to form a layer of solute molecules on the surface of adsorbent due to force of attraction between adsorbent and adsorbate. For different adsorbents, the force of affinity of adsorbate on adsorbent surface varies,

which causes different amount of adsorption. For high rate of adsorption, the affinity of adsorbate on the surface of adsorbent must be greater than the solvent affinity. The adsorbate, having low solubility in solvent, has higher adsorption capacity on the surface of adsorbent. The rate of adsorption is determined by the rate of accumulation of adsorbate molecules from the bulk solution to active surface of adsorbent. For adsorption, the adsorbate molecules must diffuse across the solvent film to the pores of adsorbent. During the process of adsorption, the active sites with having high energy are occupied in short period and after this low energy sites are occupied by the remaining molecules of adsorbate. The determination of rate, each step are observed and slowest step is considered as the rate limiting step.

### **1.6.3 Parameters effecting adsorption**

During the adsorption of molecules on adsorbents, various factors such as initial adsorbate concentration, temperature, pH, and agitation speed, nature of adsorbent, particle size and presence of foreign ions affect the rate and extent of adsorption.

#### **1.6.3.1 Concentration**

The removal efficiency of adsorbent is affected by the initial concentration of metal and dye in the solution. The immediate contact between adsorbent and adsorbate depends on the available sites present of adsorbent. The percentage removal of dye and metals decreases due to high value of adsorbate ions in comparison to the low active sites of adsorbent but on the other hand uptake is increased due to high driving force for mass transfer at higher initial concentration of adsorbent (Yagub et al., 2104).

#### **1.6.3.2 Contact time**

The contact time is the parameter to find out the speed by which metal/dye molecule are removed from the solution. To find out the efficiency of the adsorbent at

any specific time, the removal of metal and dye are determined at different period of contact times. It is also an important parameter to investigate the equilibrium time for adsorption (Zare et al., 2016). The adsorption capacity increases by increasing the time of adsorption and it becomes maximum at the optimum time

### **1.6.3.3 Effect of temperature**

The temperature is an important parameter to investigate the amount of adsorption on the surface of adsorbent because the amount of uptake may decrease or increase in respect to the increasing temperature of solution (Argun et al., 2008). In endothermic adsorption process the adsorbate uptake increases with increasing temperature. This is due to the increased number of adsorptive sites on the adsorbent for adsorption of dye and metal. In some other case the adsorption process is exothermic in nature which causes decrease in the mobility of metal ions to the active sites of adsorbent with increasing temperature of solution.

### **1.6.3.4 pH of solution**

The pH of the solution affects the capacity of adsorption by regulating the surface charge of adsorbent as well as adsorbate (Nandi et al., 2004). In some case of adsorption, the process is favoured in the lower pH range of solution which causes adsorption of negative adsorbate ions on the surface of positive sites of adsorbent. In the lower pH range, the surface of adsorbent became protonated ( $H^+$  ions) which favours the adsorption of negative ions. On the other hand in the higher pH range ( $pH > 7$ ), the surface of adsorbent is negatively charged with  $OH^-$  ions which favours the adsorption of the positive ions of adsorbate.

### **1.6.3.5 Dose of adsorbent**

The dose of adsorbent is an important factor to find out the percentage removal and uptake of adsorbate. Generally the percentage removal of dye and metal increases with increasing amount of dosage. On the other hand the uptake of dye and metal decreases with increase in adsorbent dose after saturation of active sites of adsorbent. This is an important parameter from an economical point of view for finding the optimum dose amount and maximum uptake.

## **1.7 Adsorption mode and contacting system**

The various experimental techniques have been used by researchers to confirm the maximum adsorption capacity of dye and heavy metal. This is done by contacting the adsorbate ions and adsorbent surface by different methods like batch and continuous contacting systems.

### **1.7.1 Batch system**

The batch contacting system of a fixed amount of adsorbent is mixed with solution of adsorbate and this mixture is agitated till a desired level of removal of adsorbate from the solution is achieved. After adsorption, the adsorbent is separated from aqueous phase. The adsorbent free solution is then recycled for more removal or used as a solvent. The batch mode of adsorption process is common and easy to design for removal of heavy metal and dye from waste water and aqueous phase.

### **1.7.2 Continuous flow system**

In the continuous mode of operation, the adsorbate solution is charged with a fixed flow rate into a column using upward or downward flow. In this flow operation adsorbent surface is always in contact with the fresh adsorbate solution. After saturation

of adsorbent, the fresh adsorbent is added at top in column and saturated adsorbent is removed from bottom side of column.

## **1.8 Activated carbon and waste water treatment**

Activated carbon has recognized as the form of carbon which have the porous and large surface area (Jin et al., 2010). Activated carbon has great potential for adsorption of undesired material such as heavy metal and dye from waste water. Activated carbon has been widely used for adsorption of pollutants from the waste water throughout the world. In past years, charcoal has been used as conventional activated carbon for water purification. The cost of commercial activated carbon is high due to high cost of raw material. So a novel raw material, with high carbon content such as agricultural biomass can be utilized for the preparation of activated carbon. Many researchers have investigated different biomass for the preparation of activated carbon such as waste rice straw (Sangon et al., 2018), orange peel (Lam et al., 2017), karanj (Islam et al., 2017), sugarcane bagasse (Cronje et al., 2011), leaves of pineapple (Mahamad et al., 2015), walnut shells (Miyah et al., 2018), coconut shell (Das et al., 2015) and rice husk (Mohanty et al., 2006). Activated carbon is prepared by dehydration and carbonization of woody biomass followed by activation.

### **1.8.1 Preparation of activated carbon**

#### **1.8.1.1 Physical activation**

Physical activation is a two step process. In this method, the raw biomass is firstly pyrolyzed in the temperature range of 500-800 °C, in presence of inert atmosphere such as nitrogen or argon. After, the process of activation of raw or carbonized material is done with carbon dioxide, oxygen and steam etc in high temperature range of 600-1200 °C (Khezami et al., 2007).

### **1.8.1.2 Chemical activation**

In chemical activation method, both carbonization and chemical activation is done simultaneously. For preparation of activation carbon the raw biomass is impregnated with chemical agent such as strong acid (phosphoric acid, sulphuric acid), strong base (potassium hydroxide, sodium hydroxide) and salt (zinc chloride) .The chemically mixed sample are then carbonized in the temperature range of 400 to 900 °C (Girgis et al., 2002). In comparison to physical activation method, chemical activation method is preferred due to lower temperature and less time of activation.