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CRITICAL REVIEW ON ADSORPTION OF HEAVY METAL IONS FROM INDUSTRIAL WASTEWATER

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Abstract
Industrialization, urbanization and overpopulation have created many problems such as heavy metal ions contaminated water and the need of clean water is the utmost need in this modern era. Removal of these inorganic pollutants such as copper (Cu^{+2}), lead (Pb^{+2}), chromium (Cr^{+3}, Cr^{+6}) cadmium (Cd^{+2}), zinc (Zn^{+2}) and mercury (Hg^{+2}) ions from wastewater is necessary because they are usually carcinogenic, mutagenic and non-biodegradable in nature. Therefore, its removal is necessary to decontaminate industrial, surface as well as ground water from these hazardous pollutants. Different methods such flotation, coagulation-flocculation, reverse osmosis, photocatalytic method, chemical precipitation, ion-exchange, membrane separation, advanced oxidation and adsorption are some of the techniques for remediation of wastewater. Each method has some pros and cons, like precipitation produce sludge problem and its treatment is needed after this method. Membrane separation, reverse osmosis and advanced oxidation methods are effective but they are expensive. Fouling, scaling and periodic cleaning of membrane are some of the disadvantages of membrane separation process. Photocatalytic and electrical methods are not so mature methods. Adsorption is although a slow process but its cost-effective, eco-friendly, high specific surface area, porous structure, higher uptake, multifunctional groups and ease regeneration like properties make it a best method for removal of heavy metal ions from synthetic and industrial wastewater. In this paper adsorption, its types, adsorbents and its types, factors effecting adsorption process, adsorption kinetics, adsorption equilibrium and adsorption isotherms have been discussed.

INTRODUCTION

Water is the mostly used drink in the world for the all living organisms throughout the world. With industrialization, urbanization and overpopulation the use of water increased and its resources decreased with the passage of time. Different industries like electroplating, tanneries, agriculture, paint and pigment industries utilize large quantity of water during various processes[1]. As a result, these industries contaminate the water bodies with organic and inorganic pollutants. Organic pollutants like oils, greases, dyes and wood etc. are those pollutants which consists of C-H bonds, while inorganic pollutants are those pollutants that usually include heavy metal ions, nitrates, sulfates and phosphates coming out from numerous industries[2].

Heavy metals are those metal whose density is 4-5 times heavier than water at the same temperature and pressure[3]. Examples of heavy metal ions are zinc

(Zn^{+2}), lead (Pb^{+2}), chromium (Cr^{+3}), chromium (Cr^{+6}), cadmium (Cd^{+2}) and many more[4]. They cause various diseases in animals, plants and human being due to their non-biodegradability, mutagenic and carcinogenic nature[5]. Mercury that is toxic heavy metal cause paralysis and caused Minamata bay diseases in Japan and a lot of people died due to mercury accumulation in the gills of fish and that mercury then transferred through food chain to human beings[6] . Lead halt the photosynthesis process in plants and can cause anemia in human beings. Chromium is carcinogenic, while lead and chromium cause confusion and damage liver and kidneys[7].

There are many methods through which we can reduce or remove these toxic heavy metal ions from industrial wastewater. Some of them are precipitation, coagulation-flocculation, ion-exchange method, membrane separation method, flotation method, reverse osmosis, advanced oxidation and adsorption process. Each method has some pros and cons for example the precipitation produce sludge although it can remove heavy metal ions like copper and zinc ions[8]. Likewise, membrane is effective in the removal of heavy metal ions but it is expensive and require the capital and operating cost. Ion-exchange is expensive and create regeneration problems[9]. We will discuss the adsorption process in detail in this paper because it is cost-effective, eco-friendly, regenerable and needs less space.

Table 1. Sources and Effects of Heavy metal ions

Heavy Metal ions	Sources	Effects
Lead (Pb^{+2})	Steel and batteries industries	Headache, Learning difficulties
Cadmium (Cd^{+2})	Coal, Ni-Cd batteries	Bone pain
Copper (Cu^{+2})	Pipes, cooking pots	Anemia, Heart problems
Chromium (Cr^{+6})	Tannery and Steel industries	Cancer, liver and lung damage
Mercury (Hg^{+2})	Paper and Pulp industries	Tooth decay, deafness

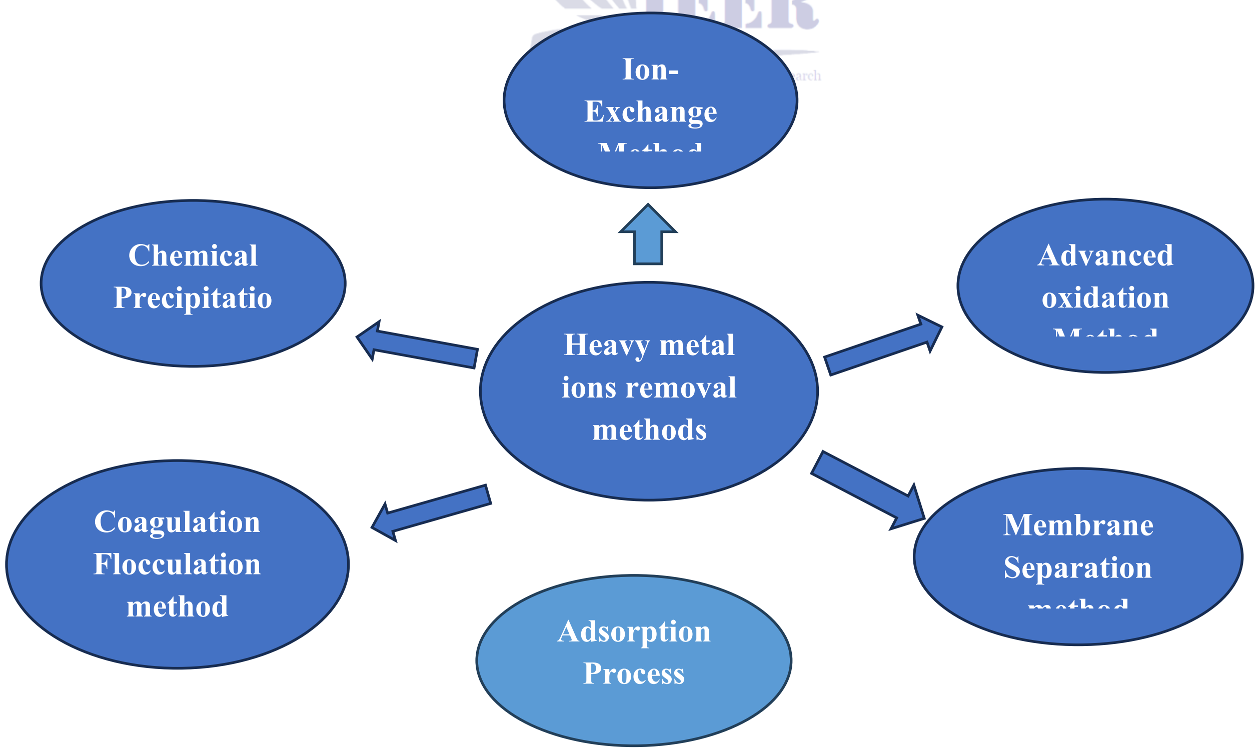

Fig 1. Heavy metal ions removal methods

2. Heavy metal definition and their toxicity

2.1. Chromium

Chromium is hard and grey color metal that exists in different depth of the earth. There is various oxidation state of chromium but Cr (III) and Cr (VI) are the most stable and toxic states respectively. Chromium (VI) is carcinogenic and mutagenic in nature. The word carcinogenic means that it can cause cancer disease, while mutagenic means that it can change the chemical structure of DNA molecules of human beings. Permissible limit of chromium in water is 0.05ppm according to World Health Organization (W.H.O), and 0.1ppm according to Environmental Protection Agency (EPA)[10-11].

2.2. Lead

It is bluish in color and mostly occurs in divalent form. Lead disturbs the photosynthesis process in plant and can exchange other monovalent Na^{+1} ions and Ca^{+2} divalent ions. It comes out from lead batteries industries and creates diseases like anemia, vomiting, headache and learning difficulties. Waste black tea particles can remove Pb^{+2} ions from wastewater with great effectiveness. The permissible limit of lead in water according to W.H.O is 0.05ppm[12-13].

2.3. Copper

Electroplating, paper and pulp industries, corrosion and metallurgical processes discharge large amount of copper metal ions into water environment. Worker exposed to copper spray are mostly affected by lung cancer. It is the 26th most abundant elements in the earth crust and people use it from thousands of years. Similarly, Wilson's disease can also occur from the exposure of this metal ions. In this disease the body parts become unable to remove the extra copper from liver, brain and other parts of the body as a result the weakness, pain and personality of a person changes[14-15].

2.4. Mercury

It is one of the toxic heavy metals that exists both in liquid and gaseous form. Mercury is use in thermometer due to its high sensitivity of heat. It can cause paralysis in human beings in which we cannot move our body parts easily. In Japan a disease called Minamata bay disease occurred due to the accumulation of mercury in the fish gills. That stored mercury then transfer from fish to humans through food chain and paralyzed thousands of people. It is bio accumulative and can destroyed the chromosomes of our body[16].

3. Methods for the removal of heavy metal ions

There are enormous methods that can be used to remove heavy metal ions contamination from wastewater. Some of them are as under chemical precipitation, ion-exchange, coagulation-flocculation, flotation, membrane separation, reverse osmosis, advanced oxidation and adsorption process.

3.1. Chemical precipitation method

It is one of the mature and highly effective method to remove heavy metal ions like Cu^{+2}, Ni^{+2}, Pb^{+2}, Zn^{+2}, and Cr^{+3} from industrial wastewater. It depends on the pH of solution, amount of dosage and nature of pollutant. Although this method is simple but it creates large amount of sludge and its dewatering and disposal are usually difficult. There are two types of precipitation that is hydroxide and sulfide precipitation.

3.1.1. Hydroxide Precipitation

In this method hydroxide of calcium or magnesium react with soluble metal ions and forms insoluble precipitate, that can then be removed by sedimentation method. The following reaction shows the general mechanism of hydroxide precipitation method.

$$M^{+2} + 2(OH)^{-} \rightarrow M(OH)_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

whereas M^{+2} and OH^{-} represent the dissolve metal ion and precipitant respectively. For example, calcium ions can be removed by equation 2.

$$Ca^{+2} + 2(OH)^{-} \rightarrow Ca(OH)_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

3.1.2. Sulfide precipitation method

In this method the removal efficiency is high as compared to hydroxide precipitation method because the solubility of metal in this method is small and works on wide range of pH. In this method the iron sulfide reacts with acidic ions and form hydrogen sulfide gas and iron ion. The hydrogen sulfide gas then treated with metal ions and form insoluble precipitate of heavy metal ions[17–19]. The whole mechanism is given by reaction 3 and 4.

$$FeS_{(s)} + 2H^+{}_{(aq)} \rightarrow H_2S_{(g)} + Fe^{+2}{}_{(aq)} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots. (3)$$
$$M^{+2}{}_{(aq)} + H_2S_{(g)} \rightarrow MS_{(s)} \downarrow +2H^+{}_{(aq)} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (4)$$

3.2. Ion exchange method

It is a reversible chemical treatment process for removal of heavy metal ions like zinc, copper, chromium, nickel and cadmium ions from industrial wastewater. There are two types of ion-exchangers, one is anionic exchanger while the second one is cationic exchanger. The former exchange their anion with anion presents in wastewater, however the later exchange their cation with cations presents in water. The ion-exchanger exchangeable ions are less harmful as compare to the ions that we want to remove. The material of ion-exchanger can be natural like natural resin or synthetic like zeolite. It is use in wastewater treatment, catalysis, sugar industries for color removal, and carbon dioxide capturing process[20-21]. Ion-Exchange mechanism is shown by the following figure 2.

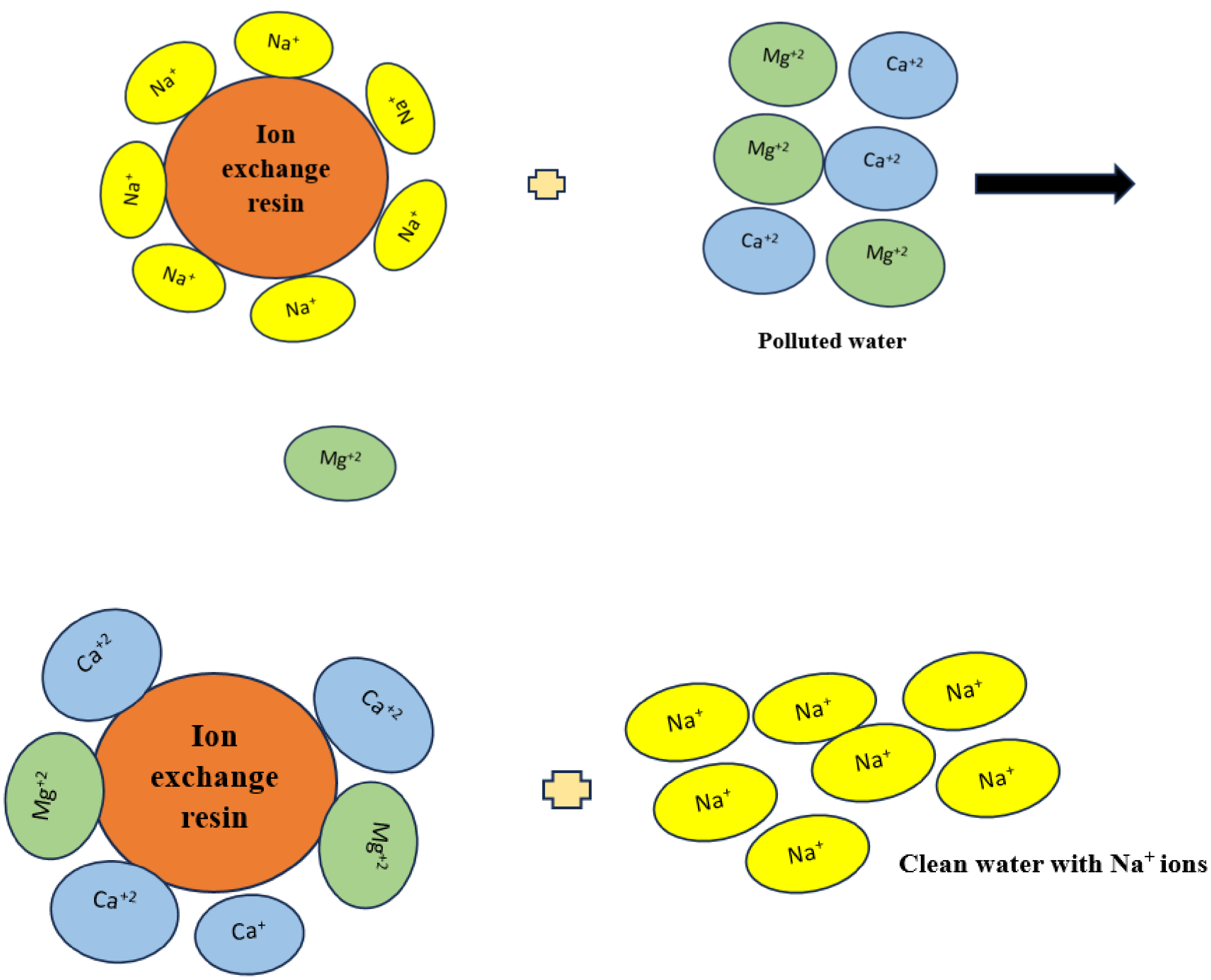

Fig 2. Ion-exchange method for removal of ions from wastewater

3.3. Flotation method

Another method to remove metal ions from dirty water is flotation method. In this method a microbubble of air pass through solution containing heavy metal ions. As the bubbles of air passes through the dirty solution, the bubbles adhere to the particles that can be heavy metal ions. As we know that the density of air is smaller than that of water so, air will transport in upward direction in the solution, will attach to the particles and will travel the particles to top of the solution. At last, the attached air plus heavy metal ion particles will remove as a sludge from the top of the solution. There are two types of flotation method, the first one is air flotation as discussed above, while the later one is precipitation flotation[22-23]. Figure 3 indicates the general air-flotation method for heavy metal ions removal.

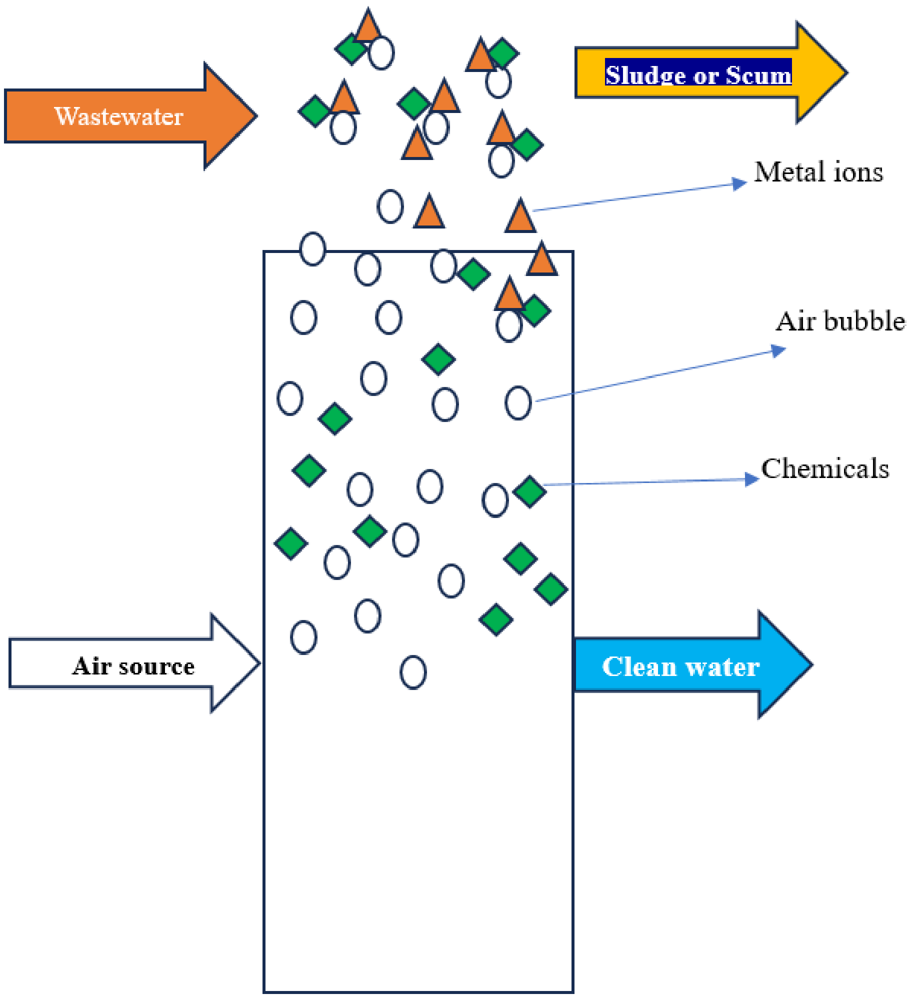

Fig 3. Air-flotation process for heavy metal ions removal

3.4. Membrane separation method

It is a barrier to separate some components while pass other. In membrane separation process the pollutants can be separated either by pressure gradient or electrical gradient. Various types of membrane are microfiltration, ultrafiltration, nanofiltration, reverse osmosis[24]. The first one can remove oil and suspended particles of water, 2^{nd} one can remove surfactants molecules, 3^{rd} one can remove the multivalent ions, while last one removes the monovalent ions. These names are usually given by the pore size of the membrane materials. We will explain the reverse osmosis in detail in this paper. Reverse osmosis is that type of membrane whose pore sizes is in range of 0.5-1.5nm. Their efficiency to remove heavy metal ions is from 95-99% but main drawbacks are membrane fouling and degradation with the passage of time. Reverse osmosis process can remove nickel, chromium and copper ions from electroplating industries wastewater with greater than 98% efficiency[25-26]. Figure 4 shows the general membrane separation process for heavy metal ions removal.

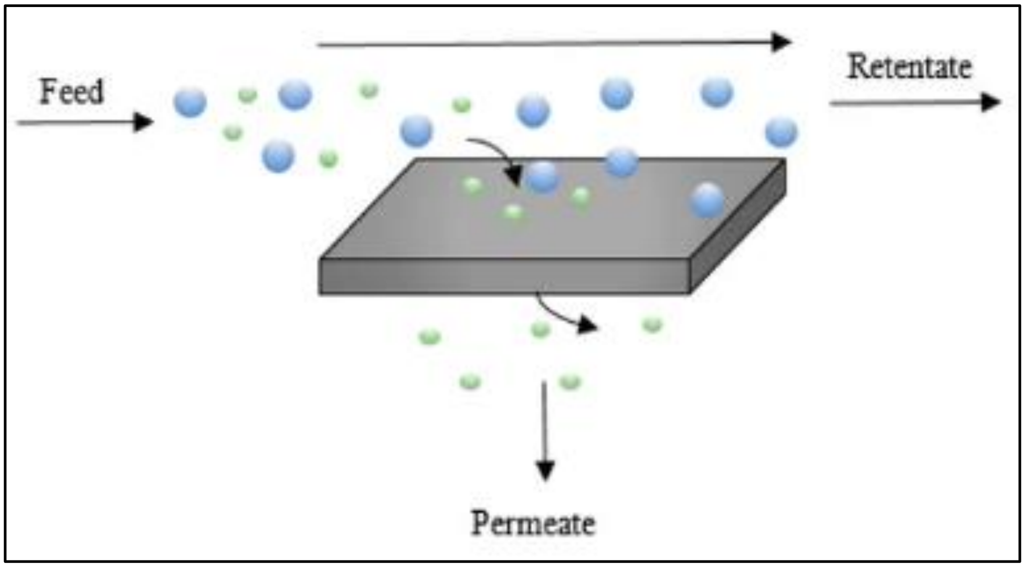

Fig-4 membrane separation method for wastewater treatment

3.5. Coagulation and Flocculation method

The colloidal particles are usually stable in solution because strong repulsive forces are present among them. Chemical that is aluminum sulfate, aluminum chloride, alum, iron sulfate and iron chlorides are added to destabilize the colloidal particles. Once the particles destabilize, after that we add chemicals like polymer, polyacrylamide etc. that surrounds the micro flocks and make macro flocks that then easily settle down to the bottom due to gravity. Heavy meat ions like copper, nickel, lead and chromium can be easily removed by this method but the removed sludge can hazardous and non-bio-degradable in nature[27-28].

3.6. Advanced oxidation process

These are processes which are used to remove organic as well as inorganic pollutants from wastewater. In these processes the hydroxide radicals are producing and that radicals then degrade the contaminants to less harmful chemicals. They can Fenton process, ozone-based process, photocatalysis, H_2O_2-UV and solar photocatalytic process. In solar photocatalytic process we degrade organic compounds from wastewater with the help of radical especially OH^- to harmless compounds such as water and carbon dioxide[29]. TiO_2 is mostly used catalyst in presence of UV light, O_2 and water for production of OH^- radicals. When light that is equal or greater than catalyst's band gap energy falls on the catalyst particle it transfers electron from valence band to conduction band and create hole in valence band. The electron as a negative charge interacts with oxygen molecule and forms negative charge. While the hole contact with pollutant of water and produced harmless water and CO_2 as shown by the following equations as well as figure 5.[30-32].

$$TiO_2 + hv \rightarrow h^+ + e^- \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (5)$$
$$h^+ + OH^- \rightarrow OH^- \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.\ldots.. (6)$$
$$e^- + O_{2(ads)}{}^- \rightarrow O_{2(ads)}{}^- \ldots\ldots\ldots\ldots\ldots\ldots.\ldots.. (7)$$

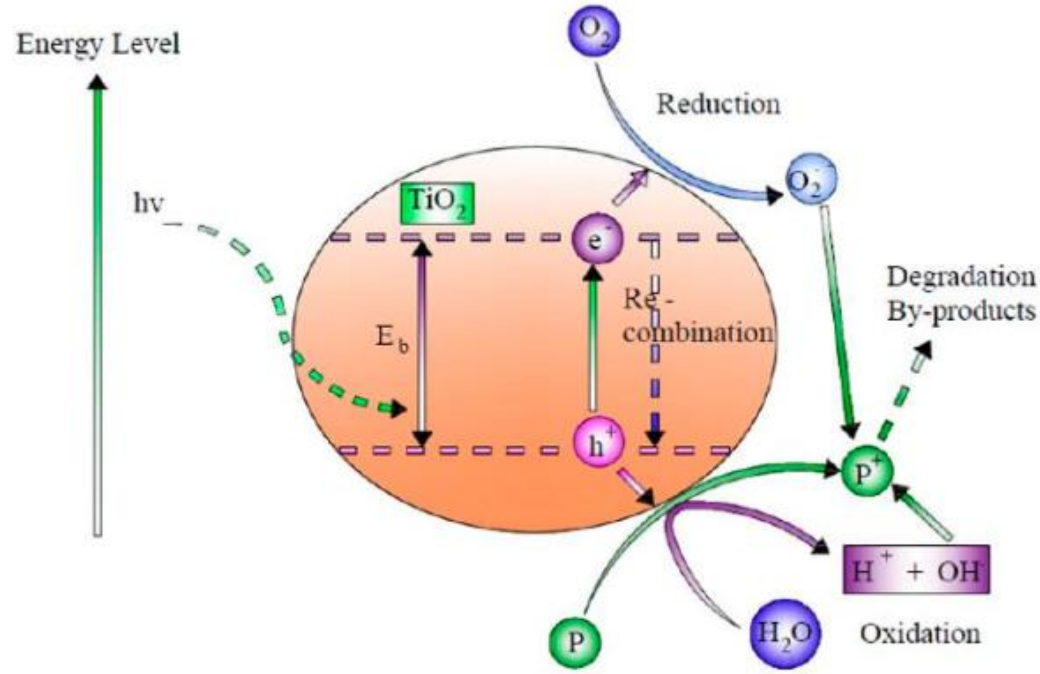

Fig 5. mechanism of advanced oxidation process[30]

3.7. Adsorption Process

Adsorption is a process in which an ion, or molecules adhering to the surface of adsorbent due to some concentration or partial pressure gradient. In liquid it is the concentration difference that provide the driving force, while for gases partial pressure gradient provide the driving force for adsorption process[33]. The ions, or molecules are usually called the adsorbate, while the material on which they are attaching are known as adsorbent. The adsorption mechanism is very simple and consists of the following steps.

Step 1: The diffusion of adsorbate from bulk solution to the surface stagnant layer surround the adsorbent particle due to some driving force. That can be partial pressure, concentration or mole fraction for gas and liquid phase respectively.

Step 2: Diffusion of adsorbate across the stagnant layer which surrounds the adsorbent. Mass transfer through this layer depends on the thickness of stagnant layer. If layer's thickness is large then resistance to mass transfer will increase, but when velocity of fluid increase then mass transfer rate will be enhanced.

Step 3: In this step the ions or molecule attached to the adsorbent surface due to some physical or chemical forces. In physical adsorption it is the weak Vander wall force of attraction between adsorbate and adsorbent, while in chemical adsorption it is the chemical bond which is mainly responsible for the adsorption of adsorbate. The chemical bonds that can be covalent or coordinate covalent bond that are mainly responsible for chemical adsorption process.

Step 4: In this step the ions or molecules or adsorbate then migrates inside the pores of adsorbent. Knudsen diffusion inside the pores of adsorbent particles depends on the inside fluid, its density, pore diameter and nature of adsorbent. This step is called intraparticle diffusion, various model like Weber Morris model is used to determine the intraparticle diffusivity of the adsorbate inside adsorbent pores.

Step 5: In this step some of the adsorbate adhere inside the pore of adsorbent, while some of the adsorbate particles can desorb and come out from the adsorbent particles, which is called desorption[34,35].

4. Types of adsorptions

Actually, there are two types of adsorptions. First one is physical adsorption, while the second is chemical adsorption.

4.1. Physical adsorption

In physical adsorption there is a weak Vander Waal force of attraction between adsorbates and adsorbent.

These forces can be weak or break by high temperature or low pressure. So, once we increase temperature or decrease pressure the adsorbates ions, or molecules can be desorbed from adsorbent particle. Physical adsorption is a reversible process with low enthalpy change (20-40kj/mol)[36].

4.2. Chemical adsorption

It is a type of adsorption in which chemical bond is responsible for adsorption of adsorbates. The chemical bond can be covalent or co-ordinate covalent bond. Desorption of ions, or molecules in this type of adsorption is not very easy. Sometime a leaching agent like EDTA can be used to desorbed these adsorbates from adsorbent. It is an irreversible process with high enthalpy change (80 – 240kj/mol)[37-38]. Figure 6 is about adsorbent and adsorbate interaction during adsorption process.

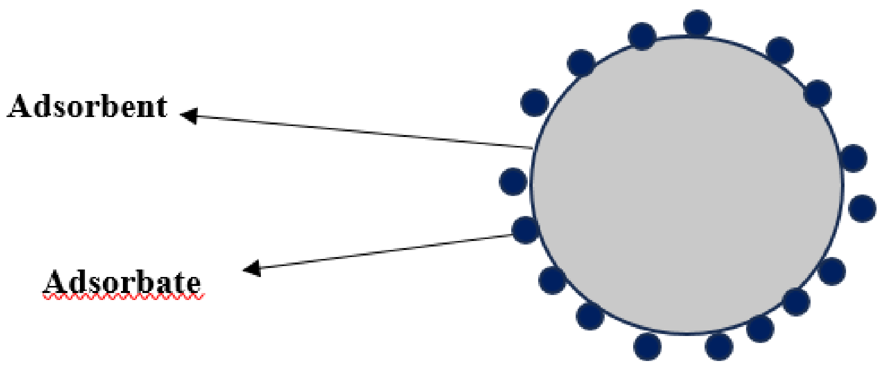

Fig 6. Adsorbate and adsorbent

5. Types of adsorbents

Adsorbents can natural or synthetic.

5.1. *Natural adsorbents*

These are usually less efficient, eco-friendly and cost-effective materials which are usually obtained from natural materials like animals or plants. Examples of natural adsorbents are rice husk, peanut shell, egg shell, potatoes peal, pea pod peal waste, animal manure, chicken leather, wood, grass, biomass and many more[39-40].

5.1.1. Sawdust

It is a solid waste generally obtained by sawmill in large quantity. It is a cheap adsorbent use for the adsorption of Zn^{+2}, Cr^{+6}, Cu^{+2}, Ni^{+2} and Pb^{+2} ions from aqueous solution. Lignin, polyphenolic, cellulose and hemicellulose are the main components of sawdust particles. These chemical compounds act as binder for heavy metal ions. Poplar sawdust modified with H_2SO_4 at 150°C increased the adsorbent uptake from 5.4mg/g to 13.5mg/g within 24 hours as reported by Mehmet Emin Argun at al. They also investigated that saw dust removal efficiency increases with pH of solution as well as with activation, as indicated by their finding that untreated sawdust removal efficiency is 47% compared to 92% removal efficiency (treated sawdust) at pH 4 and 5 respectively[41]. Chemically treated sawdust removal efficiency enhanced with pH, temperature, adsorbent dosage and followed Langmuir adsorption isotherm as investigated by Ahmad et al. HCl treated oak sawdust removal percentage for Cu^{+2}, Ni^{+2} and Cr^{+6} was 93%, 82% and 84% at pH 4, 8 and 3 respectively as reported by Argun et al[41].

5.1.2. Husk and Straw

A by-product of rice mill which consists of cellulose, hemicellulose, lignin and ash that can be applied for abatement of heavy metal ion from aqueous both in their unmodified and modified condition. Rice husk can be modified with NaOH, polyaniline, and sulfur to increase their adsorption efficiency. Similarly, wheat straw showed the same chemical composition as rice husk, used as an adsorbent for removal of heavy metal ions like Cu (II), Ni (II) and Zn (II), due to its -OH functional group. The adsorbent (wheat straw) uptake for Ni^{+2}, Cu^{+2}, Zn^{+2} was 2.49 mg/g, 4.9 mg/g and 3.23mg/g respectively as indicated by researchers Gorgievski et al [42-43].

5.1.3. Tea waste as a low-cost adsorbent

Tea is mostly used drink in Pakistan and every day a lot of tea waste are discarded into open environment without their proper treatment. Although tea is useful in some cases like it decrease the fat level in body, it has anti-cancer properties but it creates land pollution. Tea waste cannot use directly to remove dyes or heavy metal ions from wastewater because it contains some coloring components and when we added it to wastewater their leaching occurs in water, so their proper treatment is necessary to remove these coloring components and fats from tea particles before adsorption experiments[44]. Therefore, after collection of waste tea we should washed these particles with tap and distilled water several times (7-8 times) to remove fats and coloring compounds of it. After washing, the drying of tea particles is taking place to remove water molecules from it at 70 °C for about 4- 5 hours in an oven. After that we can use the treated tea particles for adsorption experiments at lab scale. For better performance we can also reduce and separate the size of tea particles to 1mm, 0.5mm, 0.212mm and 0.3mm by pestle-mortar and sieve shaker. Tea particles consist of lignin, cellulose, hemicellulose and polyphenolic compounds that that make it great adsorbent for the adsorption of lead Pd^{+2} and chromium Cr^{+6} ions from synthetic wastewater at lab scale. Mohit Nigam et al concluded that treated black tea particles showed pseudo-second order model, for adsorption of hexavalent chromium Cr (VI) from synthetic waste water, whereas Langmuir adsorption model were best fitted as shown by their isotherms[45] .

5.1.4. Bio-char as an adsorbent

It can be obtained from the pyrolysis of biomass in oxygen limited environment at 300 - 700°C. Biomass materials are usually cheap, readily available, and environment friendly solids. Crops, woods, leaves, manure and sludge are some of the examples of biomass[46]. Different types of bio-chars are using to adsorb various heavy metal ions from synthetic and industrial wastewater. Several factors like biomass nature, specific surface area of biochar, solution pH, solution temperature, nature of adsorbates, contact time, pyrolysis temperature etc. are some of the factors that affect the adsorption process[47]. The bio-char can be modified by either physical, chemical or physio-chemical methods to increase the specific surface area and adsorbent uptake. The physical modification involves the addition of steam, while in chemical modification we use some chemical like acids, bases, and salts (HCl, HNO_3, NaOH, KOH, NaCl)[48]. Xincai Chen et al removed Zn (II), and Cu (II) ions by hardwood bio-char (prepared at 450 °C) and their uptake were 4.54mg/g, 6.79mg/g respectively[49]. Similarly, Pushpita Kumkum et al removed Pb (II) from wastewater using bagasse bio-char synthesized at 600°C pyrolysis temperature[50].

5.1.5. Peels are good adsorbents

Orange, banana, potato peels and tree barks are used from few decades to clean wastewater but due to leaching of coloring and other components their improvement is utmost need. Surface functional groups of -OH, $-NH_2$ and -COOH made them good materials for water purification from heavy metal ions like Cr (VI), Pb (II), dyes like methylene blue, methyl-orange etc. Ramakrishna Mallampati et al investigated fruit peels, of avocado, hamimelon and dragon, were tested as good bio-adsorbents for decontamination of water. The percentage removal of dyes and heavy metal ions by these peels were in range of 95-100%. Highest adsorption efficiency, of dragon fruit peel was close to 100%, toward dye (alcin blue 71.85mg/g) at normal pH of solution. Langmuir isotherm model was best fitted to the adsorption process, confirmed that electrostatic force of attraction was mainly responsible for the adsorption of adsorbate toward adsorbent[51].

5.2. Synthesized adsorbents

These are those adsorbents that can be synthesized in laboratory, activated carbon, bio-char, silica gel, activated charcoal etc. are some of the examples of man-made adsorbents. We can activate the adsorbents to enhance their adsorption uptake, adsorption efficiency, increase the number of functional groups on their surface. The adsorbent activation can be physical like activation with steam, while in chemical activation we added some chemical like H_2SO_4, HCL,

$KMNO_4$, NaOH, KOH, CH_4 to increase the adsorbent uptake[52].

6. Adsorption Kinetics study

Adsorption kinetics describe the mechanism of adsorption and adsorbent uptake at fluid-solid interface. Basically, there are various steps involve during the adsorption of heavy metal ions from wastewater like external diffusion, surface reaction and intraparticle diffusion. Adsorbent kinetics depend on the physical, chemical properties of the adsorbent and adsorbate along with environmental conditions. Lagregren proposed an equation for the adsorption kinetics that are pseudo-first order and pseudo-second order kinetics models to compare the experimental data with kinetics model. The differential and integrated equations for pseudo-first order model is given by equation 8 and 9 respectively.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(8)$$

After Integration and applying limit to above equation will get equation 9.

$$\ln(q_e - q_t) = \ln(qe) - k_1 t \ldots\ldots\ldots\ldots.(9)$$

At time $t = 0,\ q_t = 0, at\ \ time\ t = t, q_t = q_t$

Whereas $q_t(\frac{mg}{g})$ is adsorbent uptake a time t(min), $q_e(\frac{mg}{g})$ is the adsorbent equilibrium uptake that can be determine from y-intercept of the line. And k_1 is rate constant of pseudo-first order equation that can be obtained from slope of the line. The mathematical form of pseudo-2nd order kinetic model is given by equation 10.

$$\frac{dq_t}{dt} = k_1(q_e - q_t)^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(10)$$

After applying integration and limit the linear form of pseudo-2nd order kinetic model is given by equation 11.

$$\frac{t}{q_t} = \frac{1}{(k_2)(q_e)^2} + \frac{t}{q_e} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(11)$$

Whereas t is time of adsorption experiment, q_t is adsorbent uptake at any time t, q_e is equilibrium uptake, $k_2(\frac{g}{mg.min})$ is rate constant of reaction[53–55].

According Mesfin Yimer et al Cd^{+2}, Cr^{+3} and Pb^{+2} adsorption by cobalt-diphenyl complex is best fitted to pseudo-second order kinetic model with regression coefficient R^2 = 0.994, 0.997 and 0.995 for cadmium, lead and chromium respectively[56]. Similarly, M.Manjuladevi et al synthesized an activated carbon from Cucumis melo pee to adsorb cadmium Cd (II) ions from 100ppm solution of Cd (II) ions and conformed correlation coefficient R^2 = 0.99, q_e = 7.22, k1 = 0.015 and y-intercept log(q_e) = 1.97 for pseudo-first order model and concluded that pseudo-first order model is best fitted to experimental data[57]. Amal A investigated the removal of Fe (III) and Mn (II) from aqueous solution using activated carbon as an adsorbent for their removal and concluded that pseudo-second order kinetic model is best fitted to the experimental data as compare to pseudo-1st order model due to higher correlation coefficient (R^2 = 0.81 Pseudo-1st, R^2 = 0.99 pseudo-2nd)[58]. According to Tumampos et al the experimental and calculated uptake of lead and copper ions are very close to each other and best follow the pseudo-second order kinetic model ((Cu^{+2}(q_{e-exp}) (mg/g) = 56.74, q_{e-cal} = 53.82)), Pb^{+2}((q_{e-exp}) (mg/g) = 99.80, $q_{e\ cal}$ = 93.74)). Their investigations show that chemical adsorption is the rate limiting step during attachment of Pb^{+2} and Cu^{+2} ions on MnO_2 due to complexation between negative hydroxide function group of adsorbent and positive metal ions[59].

7. Adsorption Isotherms

Isotherms are constant temperature curves that show that whether adsorption is favorable or not. There are numerous types of adsorption Isotherms that is Langmuir, Freundlich, Langmuir-Freundlich and Temkin adsorption isotherms.

7.1. Langmuir Adsorption Isotherm

It is one of the best adsorption isotherms to plot adsorption equilibrium data of experiments. It assumes that monolayer is formed on the surface of homogenous adsorbent surface as well as there is no interaction between adsorbed atoms, molecules or ions. Also, one active site is responsible for adsorption of a substance is also assumed in this model[60]. Its mathematical form is represented by equation 12.

$$q_e = \frac{(q_m)(k_l)(C_e)}{1 + (k_l)(C_e)} \dots\dots\dots\dots\dots\dots\dots (12)$$

Whereas q_m is the adsorbent uptake when monolayer is formed, $q_e(\frac{mg}{L})$ is equilibrium uptake, $k_l(\frac{L}{mg})$ is Langmuir constant and $C_e(\frac{mg}{L})$ is the equilibrium concentration. According to Faith et al the equilibrium study of copper and lead ions adsorption best follow the Langmuir adsorption isotherm as shown by their higher regression coefficient (Pb^{+2} (R^2 = 0.94, Cu^{+2} (R^2 = 0.95)) as shown by other researchers[61-62]. The removal of heavy metal ions Pb^{+2} and Cu^{+2} by the above-mentioned method is due to the interaction between positive ions and negative charge of the adsorbent[61].

7.2. Freundlich Adsorption Isotherm

It is one of the oldest empirical Isotherm for heterogenous surface that indicates that heat of adsorption decreases logarithmically when adsorbate is attaching to sorbent surface. Langmuir isotherm is shown by the following equation.

$$q_e = k_f \sqrt[n]{C_e} \dots\dots\dots\dots\dots\dots\dots\dots..(13)$$

Whereas $k_f(\frac{mg}{g})$ is the Freundlich constant, $C_e(\frac{mg}{L})$ is equilibrium concentration and n are intensity factor showing the affinity between sorbate and sorbent[63].

7.3. Temkin Adsorption model

According to this model, heat of adsorption decreases linearly as compare to Freundlich model which shows that enthalpy of adsorption decreases logarithmically. Its mathematical form is given by equation 14.

$$q_e = B_t(\ln A_t C_e) \dots\dots\dots\dots.(14)$$

Where heat of adsorption is $B_t = \frac{RT}{b_t}$, R is universal gas constant (8.314j/mol. K), T is temperature in Kelvin, b_t is Temkin isotherm constant, A_t is binding constant of equilibrium that indicates maximum binding energy in L/mg and C_e is equilibrium concentration in ppm(mg/L). The following equation shows a linear representation of the Temkin adsorption model.

$$q_e = B_t \ln A_t + B_t \ln C_e \dots\dots\dots\dots.(15)$$

In equation 15, B_t and A_t can be determine from slope and y-intercept of this linear equation[64-65]. According to Patrick et al, adsorption of Butylparaben from aqueous solution by coconut biochar activated carbon follow Langmuir, Freundlich and Temkin adsorption isotherms with high regression coefficient $R^2 > 0.9$ that obey pseudo-second order kinetic model[66]. Fig leaf activated carbon is a best adsorbent for methylene blue dye separation from an aqueous solution inclined toward monolayer Langmuir isotherm with maximum uptake, q_{max} = 69.93mg/g, Langmuir constant K_L = 0.08L/mg and correlation coefficient R^2 = 0.959 [67]. Similarly Jackfruit peel derived biochar is a best material for adsorption of cadmium, lead, iron and cooper ions from aqueous solution and follow Langmuir adsorption isotherm in case of copper Cu(II) ions adsorption(R^2 = 0.9966, K_L =0.11 L/mg, q_{max} = 17.5 mg/g), while Freundlich adsorption is best fitted to the adsorption of iron Fe(II) ions (R^2 = 0.9599, n =0.007, K_f = 5.067 $\left(\frac{mg}{g}\right)\left(\frac{L}{mg}\right)^n$[68].

8. Adsorption thermodynamics

The thermodynamics of adsorption process is best studied with Gibb's free energy, ΔG°, enthalpy and entropy change by the following equation 16.

$$\Delta G^o = \Delta H^o - T\Delta S^o \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (16)$$

In similar way, the relationship between distribution coefficient (rate constant) K and Gibb's free energy is given the following equation 17.

$$\Delta G^o = -RT \ln K \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (17)$$

By comparing the above equation 16 and 17 we will get equation 18 and 19.

$$-RT \ln K = \Delta H^o - T\Delta S^o \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.\ldots\ldots (18)$$

$$\ln K = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (19)$$

Equation 19 is called Vont Hoff equation which is used to determine the enthalpy ΔH^o and ΔS^o from slope $\frac{-\Delta H^o}{RT}$ and y-intercept $\frac{\Delta S^o}{R}$ of the equation 19 as given above[69-70].

According to Benny Marie et al adsorption of copper Cu^{+2} and lead Pb^{+2} by adsorbent MnO_2 is spontaneous, endothermic and $\Delta S^o > 0$ means that randomness of ions during solid-liquid is slightly increased[71]. Similarly, Patrick et al conformed that the adsorption of Butylparaben on coconut biochar derived activated carbon is non-spontaneous, disorder and endothermic physical adsorption with $\Delta H^o = 0.2 \frac{J}{mol}$ and $\Delta S^o = 19.0 \frac{J}{mol.K}$ respectively[66]. According to Safaa Talib et al adsorption of methylene blue dye from aqueous solution by Fig leaf activated carbon is spontaneous, endothermic and disorder process as conformed by their $\Delta G^o = -6.47 \frac{kj}{mol}$, $\Delta H^o = 49.3 \frac{kj}{mol}$ and $\Delta S^o = 190.33 \frac{J}{mol.K}$ at $T = 293K$[67].

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